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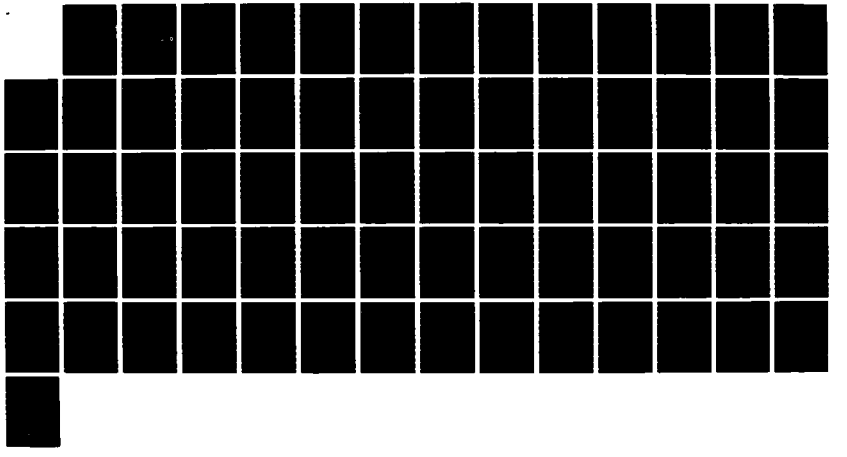

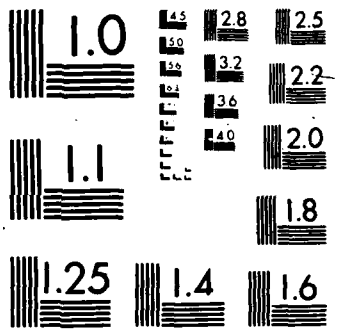
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AVAILABLE FIELD METHODS FOR RAPID SCREENING OF HAZARDOUS WASTE MATERIALS AT WASTE SITES

AD-A172 544

Final Report

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Laura Mangoba
Edward T. McHale

June 1983

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The objective of this study was to perform preliminary laboratory evaluation of as many of the selected Class A poison detection techniques as possible within the time constraints of the program. Each of these methods was tested, when possible, for their limits of detection, reproducibility of test results, accuracy, maximum sample volume necessary, and cross sensitivities to other Class A poisons. The methods to be evaluated were for arsine, hydrogen cyanide, cyanogen chloride, nitric oxide, nitrogen dioxide, lewisite, phosgene, mustard gas, and phosphine.

FOREWORD

PREFACE

Much attention has been focused on the hazards of chemical waste disposal. Many of the disposal practices that were acceptable twenty years ago are now subject to much criticism. This is primarily due to technology being better able to define the environmental impact of past disposal processes. The main concern today is the protection of the health of the people and the environment around these chemical dumping sites. In many cases, urban development has precipitated the current problem by expanding into regions too close to these disposal sites. Resolution of suspect chemical storage problems generally requires that such sites be cleaned up or recontainerized so that the chemicals do not pose a threat.

A significant problem associated with the removal of materials from these sites is that of personnel safety. The relative toxicity of the material is unknown and, therefore, could present a significant health hazard. Substances having the physical and toxicological characteristics of Class A poisons could prove instantaneously fatal to waste handlers if inhaled in sufficient concentration for a brief period. A Class A poison is defined as an extremely dangerous poisonous gas or liquid of such a nature that a very small amount of gas or vapor of the liquid mixed with air is dangerous to life. The opening of sealed containers at waste sites, containing unknown substances, presents a situation where exposure to high concentrations of these materials could occur. For safety considerations, the presence or absence of chemicals which have the characteristics of Class A poisons should be established prior to the routine handling of unknown substances at waste sites. In addition, special shipping requirements must be met before these substances may be legally transported.

It is desirable, therefore, to have methods for the in situ screening of these materials at waste sites prior to handling or packaging operations. The objective of this study was to evaluate the most promising field techniques for the positive identification of selected Class A poisons.

ABSTRACT

The objective of the third (present) phase of this study was to perform preliminary laboratory evaluation of as many of the selected Class A poison detection techniques as possible within the time constraints of the program. The methods evaluated for use to detect Class A poisons were selected in the first phase of this study. Each of these methods was tested, when possible, for their limits of detection, reproducibility of test results, accuracy, maximum sample volume necessary, and cross sensitivities to other Class A poisons. The methods to be evaluated were for arsine, hydrogen cyanide, cyanogen chloride, nitric oxide, nitrogen dioxide, lewisite, phosgene, mustard gas, and phosphine.

The method evaluated for the field detection of arsine was the Draeger arsine detector tube CH25001. This tube was found to be capable of detecting arsine at its TLV concentration of 0.16 mg/m^3 using a 2,000cc sample volume. In addition, at high concentrations of arsine this method appears to be capable of differentiating between various concentrations but results obtained at high concentrations are not quantitative.

The method which appeared to be the most promising for the field detection of hydrogen cyanide is the Draeger hydrogen cyanide detector tube CH25701. This tube was found to be capable of detecting hydrogen cyanide at a concentration of 5.5 mg/m^3 which is below the TLV of this gas (11.0 mg/m^3). In addition, this technique is capable of distinguishing increasing concentration of hydrogen cyanide in the range of 10 to 55.2 mg/m^3, but these results were not quantitative. Arsine, cyanogen and phosphine were found to cross interfere with this method which may indicate that this tube can be used to concurrently screen for several Class A poisons.

The technique for the field screening of cyanogen chloride, the Draeger cyanogen chloride detector tube CH19801, could not be evaluated for its limits of detection because of the immediate unavailability of cyanogen chloride. Cross sensitivities to other Class A poisons were investigated and it was discovered that nitrogen dioxide would give a positive reaction at concentrations of 18.4 mg/m^3.

The Draeger nitrous fumes detector tube CH29401 appeared to be a promising technique for the field detection of nitric oxide. Laboratory testing of this tube indicated that 1.67 mg/m^3 of nitric oxide could be detected using a 500cc sample volume. The limit of detection for nitric oxide is well below the 31.25 mg/m^3 TLV concentration of this gas. Increased concentrations of nitric oxide, up to 56.4 mg/m^3, were detected using 100cc sample volumes. It was found that the results obtained when using a reduced sample volume (100cc) were not quantitative. However, the detection tube was capable of indicating increasing concentrations of nitric oxide.

The method which appeared to be the most promising for the field detection of nitrogen dioxide was the Draeger nitrogen dioxide detector tube CH30001. Concentrations of 1.77 mg/m^3 of nitrogen dioxide were detected during the laboratory evaluation of this technique using a 500cc sample volume. The TLV concentration for this gas is 9.0 mg/m^3. Samples containing as much as 46.0 mg/m^3 were also detected using a 200cc sample volume. Results from the detection capability testing indicate that this tube will detect semi-quantitatively concentrations from 1.67 to 20 mg/m^3. However, when concentrations are in excess of 20 mg/m^3 data obtained using this technique are not reliable quantitatively, though nitrogen dioxide is detected. In addition, no other Class A poison tested cross-interfered with this tube.

The Draeger lewisite and arsine detector tube CH26303 will detect these compounds in addition to methyldichloroarsine, ethyldichloroarsine and phosphine. Atlantic Research Corporation was not able to investigate the detecting limits of this tube for lewisite, methyldichloroarsine or ethyldichloroarsine because of the unavailability of these chemicals. However, it was determined that arsine could be detected at 10 mg/m^3 and phosphine at 6.1 mg/m^3 using an 800cc sample volume. Neither of the gases was detected at its TLV concentration. Cross sensitivity testing conducted with this tube using the remaining Class A poisons gave negative results.

Phosgene can be detected in the field by using the Draeger phosgene detector tube CH19401. The manufacturer also states that this tube will detect diphosgene with the same sensitivities as phosgene. This laboratory was able to detect phosgene at its TLV concentration of 0.41 mg/m^3 using a 1,600cc sample volume. Concentrations as high as 4.05 mg/m^3 were also detected with this technique using a 200cc sample volume. The only other Class A poison which interfered with this method was nitrogen dioxide at a concentration of 82.8 mg/m^3 with a sample volume of 1,400cc.

Mustard gas can be detected with the Draeger S-mustard detector tube CH2803. The detection limits of this tube were not verified because of the unavailability of mustard gas. Cross sensitivity testing to other Class A poisons was investigated and it was found that phosphine would react positively at concentrations of 6.1 mg/m^3 but not at its TLV of 0.61 mg/m^3.

The Draeger phosphine detector tube CH31101 appeared to be a promising method for the field detection of this gas. The TLV concentration of 0.43 mg/m^3 was detected with this tube using a sample volume of 1,000cc. Concentrations as high as 53.0 mg/m^3 using a 100cc sample volume were also detected by this technique. However, accuracy tends to decrease as gas concentrations increase. The only Class A poison which was also detected by this tube was arsine, which was detected at its TLV concentration of 0.16 mg/m^3 using a 1,000cc sample volume.

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SECTION 1

INTRODUCTION

The Environmental Protection Agency has focused much attention on the hazards of chemical waste disposal. Many of the approaches and practices that were acceptable twenty years ago are now subject to much criticism. This is primarily due to technology being better able to define and assess the environmental impact of past disposal procedures. Of current interest is the potential damage to ground water and populated areas created by past dumping of chemicals at waste disposal sites. Resolution of these chemical storage problems generally requires that the chemicals present be cleaned up or recontainerized so that they do not pose a threat to the environment.

A significant problem associated with the removal of samples and handling of unknown wastes in sealed containers is that of personnel safety. This is because the relative toxicity of the container is unknown and, therefore, could present a significant inhalation health hazard. For example, if a vessel contained a Class A poison, one breath of the vapors could prove lethal to a waste handler. A Class A poison is defined as an extremely poisonous gas or liquid, whose vapor when mixed in small amounts with air, is dangerous to life. For safety considerations, the presence or absence of Class A poisons at these sites should be established immediately. In addition, special shipping regulations are legally required before these substances may be transported. Therefore, before a waste can be shipped for any purpose, the shipper must know what hazard category in which to place the waste. It would be beneficial to have simple, rapid methodologies available for the field identification of Class A poisons in waste materials.

The overall study was divided into three distinct phases. The first phase dealt with identifying those substances which are defined as Class A poisons. A second objective of the first phase was to identify candidate field detection methods for selected Class A poisons, but not to perform actual laboratory studies. The first phase of the study is documented in a report, "Available Field Methods for Rapid Screening of Hazardous Waste Materials at Waste Sites: Class A Poisons", which is currently in press.

The second phase of the program involved a literature study designed to identify substances not specifically defined as Class A poisons but which have the physical and toxicological properties of these poisons. A second objective of the second phase of effort was to determine if these type substances could potentially exist at hazardous waste sites. This was documented in "Available Field Methods for Rapid Screening of Hazardous Waste Materials at Waste Sites: Survey of Toxic Wastes", which also is in press.

During phases one and two the presence of both Class A poisons and substances not specifically defined as Class A poisons but equally as toxic

were positively identified as being present at hazardous waste sites. Thus, it was determined that a situation exists at hazardous waste sites which could result in death due to inhalation hazard.

The third phase of this study was to perform preliminary laboratory studies on as many of the candidate Class A poison field detection methods as possible within the duration of the program. This report documents the results of the third phase of the study.

All three phases of the study were performed by Atlantic Research Corporation from December 1980 to October 1982 under Contract No. DAMD17-78-C-8075 with the United States Army Medical Research and Development Command. The program was funded by the USEPA tnrough interagency agreement AD-21-F-1-304-0 with the United States Army.

SECTION 2

CONCLUSIONS

As a result of the experimental studies performed during this program the following conclusions have been verified.

(1) Gas detector tubes are available for sampling headspace gases at or below the TLV for the following Class A poisons:

- Arsine
- Hydrogen cyanide
- Nitric oxide
- Nitrogen dioxide
- Phosgene
- Phosphine

(2) The following gas detector tubes exhibit cross sensitivity for other Class A poisons at the levels given below:

- The arsine gas detector tube will detect phosphine at 0.43 mg/m^3 (TLV).
- Cyanogen chloride gas detector tube will detect nitrogen dioxide at a level of 18.4 mg/m^3.
- The dichlorodiethyl sulfide (mustard gas) detector tube will detect phosphine at 6.1 mg/m^3.
- The hydrogen cyanide gas detector tube will detect arsine at 10 mg/m^3, cyanogen at 106.4 mg/m^3, and phosphine at 0.61 mg/m^3.
- The phosphine gas detector tube will detect arsine at 0.16 mg/m^3 (TLV).

(3) In general, gas detection tubes can differentiate over a large concentration range by simply varying sample volumes.

(4) Gas detection tubes are amendable to field screening of headspace gas for Class A poisons for the following selected reasons:

- Commercially available
- Pre-packaged sealed units
- No reagent chemical preparation
- Known shelf life
- Minimal training required for use
- Inexpensive
- Immediate results
- Compact

SECTION 3

RECOMMENDATIONS

The use of specific gas detector tubes for the field screening of Class A poisons needs to be further investigated in the following areas:

(1) The effect of temperature on each detection tube should be investigated since this may affect overall tube performance. In a field sampling environment the detection methods would be utilized at all ambient temperature extremes.

(2) The effects of moisture and other volatile substances potentially present in waste containers must be investigated for each specific detection tube. It is known that analytical methods can be affected by extremes in sampling matrix as would be the case in sampling vessels containing unknown substances at a variety of sites.

(3) The effect of varying degrees of operator experience should be assessed to determine what level of training and practice are needed to obtain reproducible results. This is because differences in technique between individuals can have a decided effect upon the results obtained from any analytical procedure. This is particularly true in the case of a field situation, where operators with little training may be required to screen unknown wastes for Class A poisons.

(4) Field testing of validated methods should be conducted in order to insure that the methods are consistently reliable in the field. Various waste drums would be screened for Class A poisons and corresponding samples sent to a laboratory to verify the results obtained in the field. A variety of waste sites would be sampled.

SECTION 4

APPROACH

Class A poisons are by definition volatile materials; therefore, two approaches might be applied which could be used to determine if a Class A poison existed in containers of unknown content. The first and simplest method would be a direct analysis of the headspace from closed containers for the Class A poisons of interest. The other method would entail stripping the volatile species from the unknown liquid phase (with compressed air) and examining the evolved gases. Either approach would allow for greatly simplified in situ test methods to be utilized in screening for the Class A poisons. Any interference potential should be decreased by the reduced presence of the less volatile species in the sample gas stream as opposed to analyzing a liquid sample.

It was found in Phase I of this study that the current state-of-the-art for existing general detecting methods did not provide for the specific field screening for Class A poisons. General methodologies such as portable gas chromatography, organic vapor analyzers, infrared spectrophotometry and other sophisticated instrumental techniques were generally ruled out because of their inability to screen specifically for all Class A poisons in complex matrices at a given set of instrumental parameters. However, it was found that general detection methods such as infrared spectrophotometry might be used to establish the absence of selected substances within a complex sample and this information used to determine the need for additional more specific tests.

Phase I indicated that a detection method designed for each of the Class A poisons of interest to this study was the more promising approach. Emphasis was placed on those methods which were currently commercially available. It was found that a convenient method for the field screening of specific volatile substances was the use of gas detector tubes. Gas detector tubes are small cylindrical glass tubes ($\approx$ 6.4 mm O.D. x 15.2 cm L) which contain a reagent that is specific for the gas or vapor for which the detection tube is designed. The reagent is supported on a solid substrate such as silica gel. Generally the front part of the detection tube, where the sample enters, contains chemicals which scrub out potentially interfering species before they reach the detection region of the tube. When a standard volume of sample, containing the species the detection tube is designed to measure, is drawn through the tube the reagent changes color. The length of this color change in the tube is indicative of the concentration of the substance in the sample.

It was therefore concluded in the Phase I study that gas sampling would be coupled with colorimetric gas detection tubes for the screening of Class A poisons in closed containers. Candidate methods were identified in Phase I and selected methods evaluated during Phase III of this program.

SECTION 5

EXPERIMENTAL

The objective of the third phase of this study was to experimentally evaluate the more promising commercially available candidate field detection methods for as many of the selected Class A poisons as possible within the time constraints of the program. The substances selected are given in Table 1 and are those designated by the Department of Transportation in Title 49, Code of Federal Regulations, as being or having been Class A poisons.

ACQUISITION OF CLASS A POISONS

Eight of the Class A poisons in Table 1 were found to be commercially available and were obtained in compressed gas cylinders as standard gas mixtures from Matheson Company, East Rutherford, New Jersey. Table 2 lists these poisons along with their actual certified concentrations both in ppm and mg/m^3. The matrix gas in each cylinder was nitrogen. These Class A poison gas mixtures were subsequently used in the laboratory evaluation of the candidate field detection methods.

Cyanogen chloride gas mixture was also found to be commercially available. However, the vendor for this substance was unable to deliver the gas immediately because their supply was depleted. The cyanogen chloride gas mixture was not received within the time constraints of the program and the order was cancelled.

Immediate sources for the Class A poisons:

- Diphosgene
- Phenylcarbylamine chloride
- Dichlorodiethyl sulfide
- Dichloro-(2-chlorovinyl)arsine
- Methyldichloroarsine
- Ethyldichloroarsine

could not be identified and were dropped from further consideration for laboratory evaluation. It appeared that many of the Class A poisons would have to be synthesized specifically for the purposes of this program.

A sample of bromoacetone (in liquified form) was received but also not utilized during this study due to scheduling difficulty within the available contractual time frame.

TABLE 1. Title 49 Class A Poisons

Arsine
Bromoacetone
Cyanogen
Cyanogen chloride
Dichlorodiethyl sulfide
Dichloro-(2-chlorovinyl)arsine
Diphosgene
Ethyldichloroarsine
Germane
Hydrocyanic acid
Methyldichloroarsine
Nitric oxide
Nitrogen dioxide
Phenylcarbylamine chloride
Phosgene
Phosphine

TABLE 2. Actual Concentrations of Class A Poisons in Standard Gas Mixtures

Poison	Concentration ppm	Concentration mg/m^3
Arsine	47.7	152.2
Cyanogen	50.0	106.4
Germane	60.0	187.8
Hydrogen cyanide	50.0	55.2
Nitric oxide	46.0	56.4
Nitrogen dioxide	45.0	82.8
Phosgene	47.0	190.3
Phosphine	45.4	63.2

GAS HANDLING SYSTEM

Dilution of the Class A poison standard gas mixtures from their original concentrations was accomplished as follows. A compressed gas cylinder of Matheson ultra high purity nitrogen was used as the dilutant gas. The cylinder was connected to a Heise CC-76452, 0-150 psi, pressure gauge and a Matheson 603 flowmeter tube with a stainless steel ball. All float flow tubes used for the gas handling system were housed in a Matheson 7412T four tube flowmeter having high accuracy valves. A constant nitrogen pressure was maintained by use of a Matheson Model 3104-580 two-stage regulator. The outlet of the flowmeter tube opened into the mixing chamber of the Matheson 7412T flowmeter which in turn was connected to an American Meter Company Model AL18 wet test meter. The quantity of nitrogen flowing through the system could therefore be measured by the wet test meter and the flowmeter. The flow rate was controlled by the valve on the flowmeter. Once an acceptable flow of nitrogen was established the amount (flow rate) of the Class A poison which was required to reach the desired testing concentration was calculated.

The Class A poison gas standard mixture cylinders were hooked up in the same manner as the dilutant nitrogen cylinder. The Class A cylinder was connected to a Heise CC-76451, 0-12 psi, pressure gauge and a 610 flowmeter tube with a glass float. The pressure of the standard gas mixtures was regulated by a Matheson Model 3800 stainless steel regulator. The regulator was equipped with a Matheson 4744 purge assembly to prevent accidental exposure to the standard gas mixtures when changing gas cylinders. The outlet of the standard gas flow meter opened into the same mixing chamber mentioned above. Calibration curves were prepared, using the wet test meter, for both Class A and nitrogen gases at varying pressures and flowmeter settings. These curves were used to obtain approximate instrument settings for actual experimental work. Once the nitrogen flow was set as measured on the wet test meter the total flow rate (nitrogen plus Class A) was calculated for the desired test gas concentration.

The addition of the Class A poison was achieved by adjusting its flow rate, using the valve on the flowmeter until the total required flow rate was obtained on the wet test meter. Once both of these flow rates were established testing was initiated. In the event that a small flow of standard gas and a disproportionately large flow of nitrogen was required to obtain the desired concentration a Varian aerograph 96-000015-00 bubble flowmeter was used to establish the proper flow of the standard gas. This was because at high nitrogen flow rates and extremely low standard gas flow rates any inaccuracy in measurement of the total flow would bias the final concentration to a significant degree. For example, trying to establish an accurate standard gas flow of, say, 110 ml/min when measured in addition to a nitrogen gas flow of 10,000 ml/min would be impossible. Therefore, in cases such as this the standard gas flow was first established by using a bubble flowmeter. The system was then reconnected to the wet test meter. The total flow rate was then measured and the actual nitrogen flow calculated by subtracting the Class A flow rate from the total flow rate. The actual concentration of the Class A poison was then calculated. A diagram of this gas handling system is given in Figure 1. A precautionary step was incorporated after testing to insure that

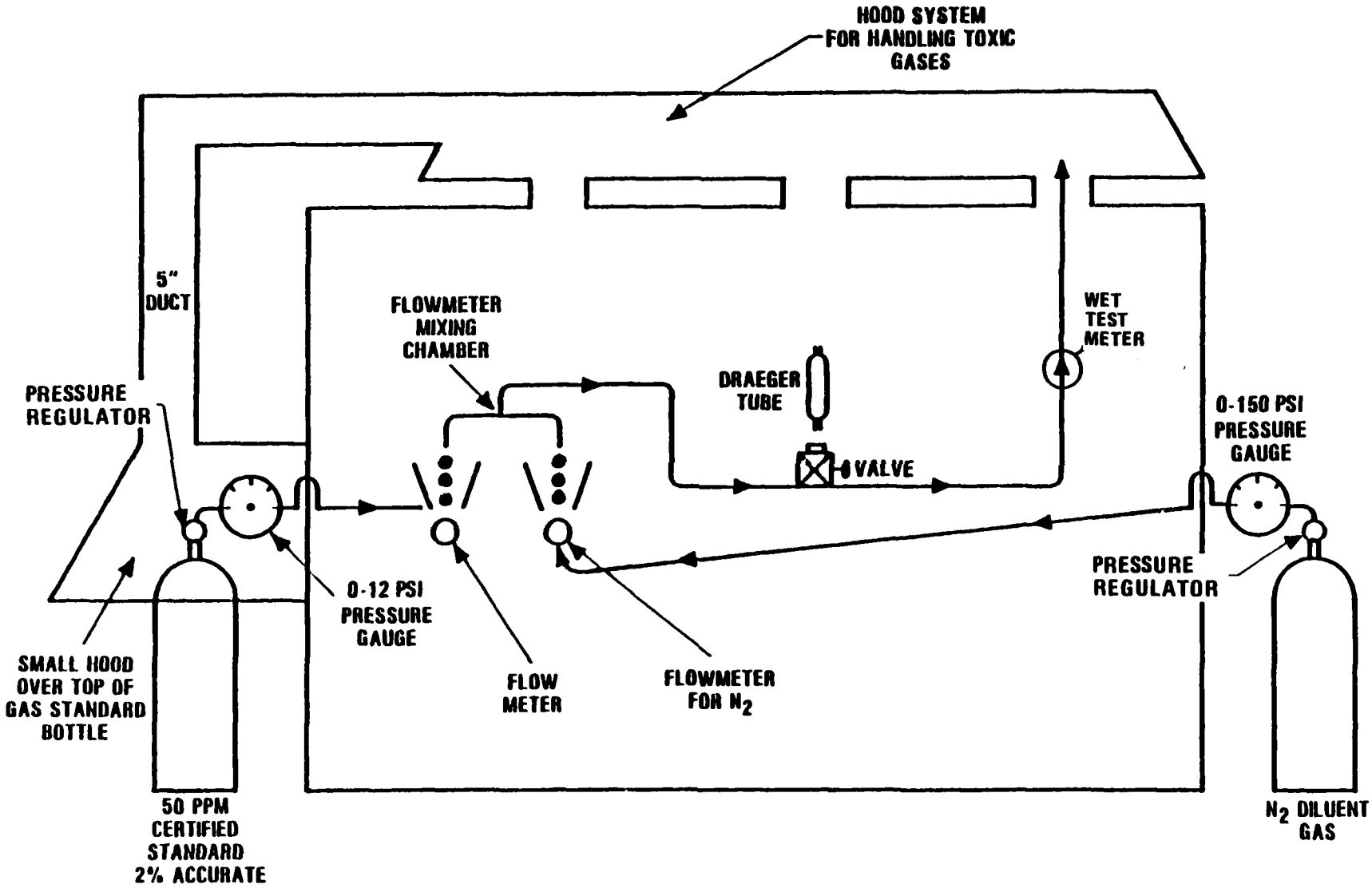

Figure 1. Gas Handling System.

the gas flow rates were maintained during testing procedures. Upon termination of testing the total flow rate was remeasured, then the Class A flow was cut off and the final flow rate (nitrogen solely) was measured. These flow rates (total and nitrogen) were then compared to the values obtained prior to testing. In all cases it was found that the flow rates were maintained during the testing phase.

ACQUISITION OF DETECTION MATERIALS.

Candidate methodologies for the field detection of Class A poisons were determined in the first phase of this study. The most promising methods were then to be evaluated in the laboratory for their potential for the field detection of Class A poisons. Eight of the most promising detection techniques were found to be commercially available and were obtained for evaluation from National Draeger, Pittsburgh, Pennsylvania. These methods are listed in Table 3. In addition to those listed in Table 3, Draeger S-mustard tube and Draeger lewisite/arsine tube, which are not sold commercially (due to lack of demand), were found to be available by special order from Draegerwerk, West Germany. These detection tubes are capable of screening for dichlorodiethyl sulfide (mustard gas), dichloro-(2-chlorovinyl)arsine (lewisite), methyl and ethyl dichloroarsine.

Reagents to manufacture gas detection tubes for the remaining four Class A poisons were not ordered due to the time constraints of the program. Intensive effort would have been required to develop detection tube techniques for the utilization of these reagents.

METHODS OF EVALUATION

Each of the methods was examined in the laboratory for lower limits of detection, reproducibility, accuracy, necessary sample volume at low gas concentrations, and cross sensitivities to other Class A poisons. Contractual time constraints did not permit interference evaluation from various substances known to be present at waste sites. In addition, the effect of environmental conditions such as temperature and humidity on testing results were not evaluated.

Limits of Detection

Sensitivity testing on each candidate detection tube method was generally conducted at the Class A poison's threshold limit value. In the event that information supplied by the detector tube manufacturer indicated a lower sensitivity than the TLV value, this lower limit was also investigated. Table 4 lists the lowest concentration tested for each gas along with its TLV value. Various other gas concentrations were also tested. These concentrations were generally selected so that the concentration range examined would contain points extending from the gases' TLV to approximately 50 ppm which was the concentration of the standard gas mixture.

TABLE 3. Commercially Available Detector Tubes

Poison	Detector Tube
Arsine	Draeger Tube CH 25001
Cyanogen chloride	Draeger Tube CH 19801
Diphosgene	Draeger Tube CH 19401
Hydrogen cyanide	Draeger Tube CH 25701
Nitric oxide	Draeger Tube CH 29401
Nitrogen dioxide	Draeger Tube CH 29401 and CH 30001
Phosgene	Draeger Tube CH 19401
Phosphine	Draeger Tube CH 31101

TABLE 4. Lowest Concentration of Class A Poisons Tested

Poison	Lowest Concentration mg/m^3	TLV mg/m^3
Arsine	0.16	0.16
Hydrogen cyanide	5.5	11
Nitric oxide	1.67	31.2
Nitrogen dioxide	1.77	9.2
Phosgene	0.41	0.41
Phosphine	0.43	0.43

Reproducibility

The ability to obtain reproducible results is critical for any testing program. In order to determine how reproducible results were for a set concentration of Class A poison, all tests were conducted in triplicate. Mean values, standard deviations, and coefficient of variances were calculated for each concentration tested. The reproducibility of each method is discussed in greater detail in Section 6 of this report.

Accuracy

The accuracy of each method examined was assessed by observing the experimentally obtained stain length on the detector tube, at a specific known concentration of a Class A poison, and comparing this length to the theoretical length that should have been obtained on the detector tube for that concentration. Values obtained from actual versus theoretical stain length were then plotted. An average percent difference was calculated between the two curves. This average percent difference was obtained by calculating a percent difference between the experimental values and the tube scale value at each experimental data point. These percent differences were then averaged to obtain one number. A discussion of the accuracy for each method tested is given in detail in Section 6 of this report.

Sample Volume

Sample volumes varied depending upon which detector tubes were being utilized and what concentration of gas was being examined. Section 6 of this report details those sample volumes used during experimentation for each specific detector tube. However, it was assumed that for detection purposes, a worst case concentration would be for the Class A poison to be present at its TLV value. Each detector tube gives a minimum detection limit for a specific volume of sample, i.e., the ability to detect a concentration of 1 mg/m^3 of a substance using a 100 ml sample volume. Therefore, the maximum sample volume required for a particular detection method would be that volume of sample which would be necessary to detect the TLV concentration for a particular Class A poison.

Cross Interference

Cross interference testing was conducted for each detector tube using every Class A poison in Table 2, with the exception of the poison for which that tube was designed. A new detector tube was used for each gas sample. The gases were first sampled at approximately 50 ppm. This concentration was chosen because it was the maximum concentration of the available Class A standard gas mixture as obtained from Matheson. If there was a positive reaction indicating an interference, a second sample was tested at the TLV concentration of the interfering gas. In the event an interference was discovered at the TLV concentration, no other testing was conducted for that gas. However, if no interference was detected at the TLV concentration, then

other concentrations were tested to determine the lower limit of interference. When no interference was obtained at 50 ppm, it was determined that the particular gas being tested did not interfere independently up to the level being tested. A detector tube's ability to detect another Class A poison other than the one for which it was specifically designed was not necessarily viewed as being undesirable. This is because if a single tube can detect 2 or more Class A poisons at their TLV limits it could reduce the amount of testing that would be required during field operations.

Sample volumes for all cross interference testing were chosen to equal the volume needed to detect the TLV amount of the gas for which the tube was designed.

Results of this cross interference testing are given for each method evaluated in Section 6 of this report.

SECTION 6

RESULTS OF LABORATORY TESTING

Arsine

The method selected in Phase 1 of this study that theoretically appears to be the most promising for the field detection of this substance is the Draeger arsine detector tube CH25001. Manufacturer's information state that this tube has a detection range of 0.16 to 9.75 mg/m^3 using a 2,000ml sample (Twenty pump strokes). The relative standard deviation according to manufacturer's literature is 15 to 20 percent depending on arsine concentration.

The initial laboratory testing of this tube was conducted at arsine concentrations of 0.16 mg/m^3, 1.6 mg/m^3, 4.5 mg/m^3, and 8.3 mg/m^3 using sample volumes of 2000 ml. The 0.16 mg/m^3 concentration corresponds to the threshold limit value (TLV) of arsine for an eight hour exposure. Each concentration was sampled in triplicate. Readings were taken according to the stain length produced as read from the preprinted scale on the tube and were also measured using a millimeter ruler. The data obtained from these three concentrations are given in Table 5 and shown graphically in Figure 2. These results illustrate that this method is extremely reproducible. The standard deviation and coefficient of variance for two of the four concentrations tested were zero. The average percent difference between the curves of experimental data and that obtained from the preprinted scale was found to be 5 percent. Figure 2 indicates that the percent difference increases with concentration, therefore, as the concentration to be detected is increased the accuracy of the tube scale decreases.

An attempt to determine how this detector tube would react to higher concentrations of arsine with a reduced sample volume was conducted. Tests were conducted at 29.0 mg/m^3, 77.5 mg/m^3, and 152 mg/m^3 using a sample volume of 100ml (1 pump stroke). Each of these concentrations were sampled in triplicate. The results of these tests are given in Table 6 and shown graphically in Figure 3. The reproducibility of the data, using one pump stroke, had standard deviations of 1.31, 0.577, and 0.115 respectively for increasing gas concentrations. The standard deviation and coefficient of variance were larger for the 29 mg/m^3 samples than the other two concentrations. The average percent difference between the experimental and preprinted curves was 16, which is significantly higher than the value calculated from Figure 2 using larger sample volumes. It would appear that it is possible to differentiate between various concentrations. However, at high concentration the method does not appear to be quantitative.

The possibility that other Class A poisons might also be detected by this tube was investigated. Samples were taken for each Class A poison

TABLE 5. ARSINE DETECTION TUBE (1 ppm = 3.19 mg/m^3)

	TEST 1		TEST 2		TEST 3		TEST 4	
Experimental parameters								
Actual test conc. (ppm)	0.05 (0.16 mg/m^3)		0.5 (1.6 mg/m^3)		1.4 (4.5 mg/m^3)		2.6 (8.3 mg/m^3)	
Number of pump strokes	20		20		20		20	
Sample volume (ml)	2000		2000		2000		2000	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3		RESULTS TEST 4	
	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
TEST DATA	0.05 (0.16 mg/m^3)	3.5	0.5 (1.6 mg/m^3)	12.5	1.3 (4.1 mg/m^3)	22	3.0 (9.6 mg/m^3)	37
	0.05 (0.16 mg/m^3)	3.5	0.5 (1.6 mg/m^3)	12.1	1.6 (5.1 mg/m^3)	25	2.8 (8.9 mg/m^3)	35
	0.05 (0.16 mg/m^3)	3.5	0.5 (1.6 mg/m^3)	12.5	1.6 (5.1 mg/m^3)	25	2.9 (9.3 mg/m^3)	36
STATISTICAL								
MEAN	$\bar{X}$ = 0.05 (0.16 mg/m^3)		$\bar{X}$ = 0.5 (1.6 mg/m^3)		$\bar{X}$ = 1.5 (4.8 mg/m^3)		$\bar{X}$ = 2.9 (9.3 mg/m^3)	
STANDARD DEVIATION	S_d = 0.0		S_d = 0.0		S_d = 0.17		S_d = 0.10	
COEFFICIENT OF VARIANCE	C_v = 0.0		C_v = 0.0		C_v = 0.11		C_v = 0.03	

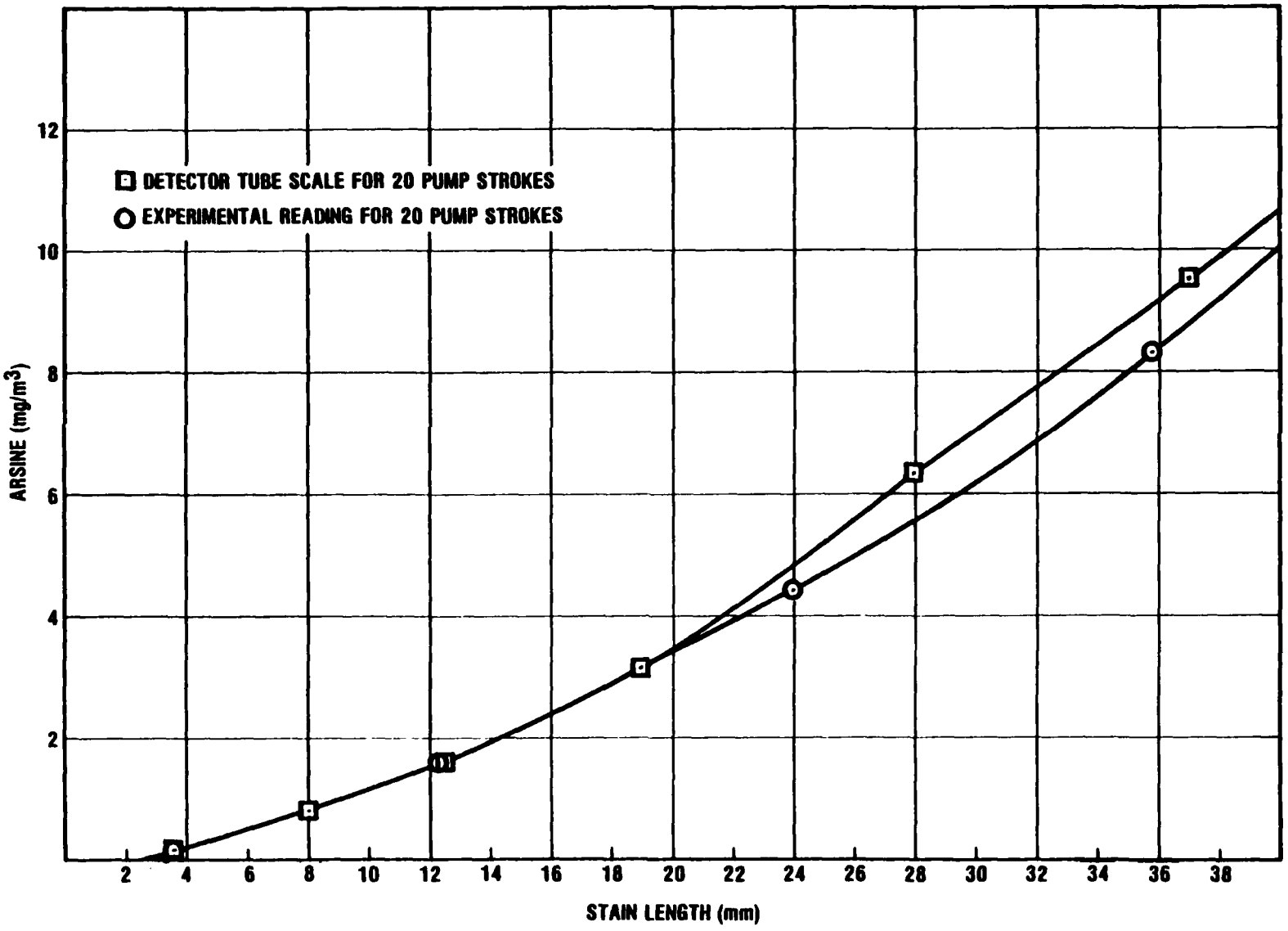

Figure 2. Stain Length Versus Arsine Concentration (with 20 pump strokes).

TABLE 6. ARSINE DETECTION TUBE (1 ppm = 3.19 mg/m^3)

	TEST 1		TEST 2		TEST 3	
Experimental Parameters						
Actual test conc. (ppm)	9.09 (29.0 mg/m^3)		24.3 (77.5 mg/m^3)		47.7 (152 mg/m^3)	
Number of pump strokes	1		1		1	
Sample volume (ml)	100		100		100	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3	
TEST DATA	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
	8.0 (26 mg/m^3)	10.5	18.0 (57.0 mg/m^3)	17	50.0 (160 mg/m^3)	33
	7.0 (22 mg/m^3)	9.5	19.0 (61.0 mg/m^3)	18	49.8 (159 mg/m^3)	32
	9.6 (31 mg/m^3)	11.5	18.0 (57.0 mg/m^3)	17	49.8 (159 mg/m^3)	32
STATISTICAL						
MEAN	$\bar{X}$ = 8.2 (26 mg/m^3)		$\bar{X}$ = 18.3 (58.4 mg/m^3)		$\bar{X}$ = 49.9 (159 mg/m^3)	
STANDARD DEVIATION	S_d = 1.31		S_d = 0.577		S_d = 0.115	
COEFFICIENT OF VARIANCE	C_v = 0.16		C_v = 0.03		C_v = 0.002	

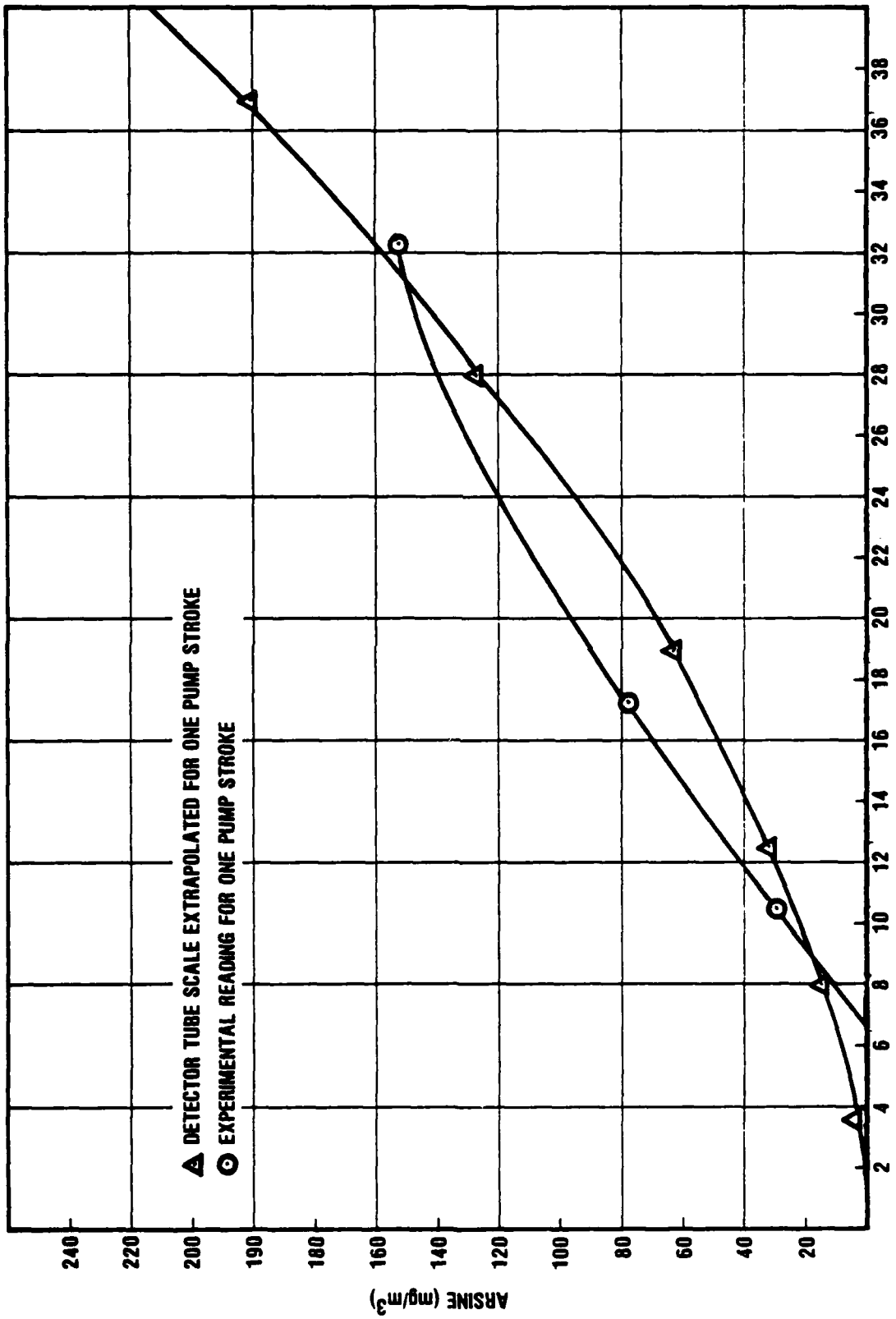

Figure 3. Stain Length Versus Arsine Concentration (with 1 pump stroke).

standard gas mixture that was available, with the exception of arsine. A new tube was used for each tested gas sample. The gases were first sampled at approximately 50 ppm. If there was a cross interference then a second sample was tested at the TLV concentration of the interfering gas. In the event a cross interference at the TLV was discovered no additional samples were tested. It was simply stated that the Class A poison interfered at its TLV and was comparable to a concentration as read from that particular tube. However, if no interference was noted at the TLV concentration other samples were then tested to determine the lower level of interferance. When no cross interferences were discovered at the 50 ppm concentration it was assumed that the particular gas would not interfere at this level with the arsine test method and no other samples were tested. The results of this cross interference testing for the arsine detector tube are given in Table 7. Phosphine was the only other Class A poison which was detected with this tube. Phosphine, at its TLV of 0.43 mg/m^3, corresponds to an arsine scale reading of 0.5 mg/m^3 (0.18 ppm) on this tube.

The data obtained during the evaluation of the Draeger arsine detector tube indicates that the method is capable of detecting arsine at its TLV concentration. In addition, it appears a wide range of concentrations may be screened by altering the volume of sample.

TABLE 7. Arsine Detector Tube Interference Data

Gas	Test Gas Concentration - mg/m^3	Interference Response
Cyanogen	106.4(50.0ppm)	No
Germane	187.8(60.0ppm)	No
Hydrogen cyanide	55.2(50.0ppm)	No
Nitric oxide	56.4(46.0ppm)	No
Nitrogen dioxide	82.8(45.0ppm)	No
Phosgene	190.3(47.0ppm)	No
Phosphine	64.5(45.4ppm)	Yes
	0.43(0.3ppm)	Yes

Cyanogen chloride

The technique which theoretically appears to be the most promising for the field screening of cyanogen chloride, which was determined in Phase 1 of this study, is the Draeger cyanogen chloride detector tube CH19801. The manufacturer's literature stated that this tube is capable of detecting cyanogen chloride in the 0.63 to 12.55 mg/m^3 range using a 100 to 2,000ml sample (1 to 20 pump strokes). There is no published TLV concentration for cyanogen chloride but it is generally agreed upon that a worker should not be exposed to any value greater than 1.26 mg/m^3 for an eight hour exposure. The reported relative standard deviation of this tube for the measurement of cyanogen chloride is 15 to 20 percent depending upon the actual concentration being measured.

Atlantic Research was unable to test this technique's sensitivity in the laboratory because of the immediate unavailability of the cyanogen chloride gas. We were, however, able to test this method for any cross sensitivities to the other available Class A poisons and this data is given in Table 8. The data in Table 8 shows that nitrogen dioxide at 18.4 mg/m^3 (10 ppm) gives a positive interference on the cyanogen chloride detector tube. At 18.4 mg/m^3 (10 ppm) of nitrogen dioxide the response of the tube is comparable to 1 mg/m^3 (0.42 ppm) of cyanogen chloride. Nitrogen dioxide, at its TLV concentration of 9 mg/m^3 (5 ppm) did not interfere with this technique.

Theoretically this tube does appear promising for the field screening of cyanogen chloride. However, laboratory work should be conducted to establish the parameters within which this tube could be used.

TABLE 8. Cyanogen Chloride Detector Tube Interference Data

Gas	Test Gas Concentration - mg/m^3	Interference Response
Arsine	152.2(47.7ppm)	No
Germane	187.8(60.0ppm)	No
Hydrogen cyanide	55.2(50ppm)	No
Nitric oxide	56.4(46.0ppm)	No
Nitrogen dioxide	82.8(45.0ppm)	Yes
	18.4(10ppm)	Yes
	9.0(4.9ppm)	No
Phosgene	190.3(47.0ppm)	No
Phosphine	64.5(45.4ppm)	No

Dichlorodiethyl sulfide (mustard gas)

The method which was initially identified as the most promising for the rapid field detection of mustard gas utilized the chemical, gold chloride. Tubes using this technique were found to be unavailable commercially. Atlantic Research Corporation was notified by Draegerwerk (Germany) that they produced a special order tube for the detection of mustard gas (CH25803) which utilizes gold chloride as the indicating reagent. This tube was obtained for evaluation purposes by special order from Draegerwerk in Germany.

The information which Draegerwerk supplied along with samples of their detector tube indicated that this method could detect 5 mg/m^3 of mustard gas using a sample volume 800ml (8 pump strokes). The only interference listed for this tube is organic compounds containing thioether groups such as tetrahydrothiophene. Because of the unavailability of mustard gas Atlantic Research Corporation was not able to verify the detection limit of this technique. It was possible, however, to test this method for any cross sensitivity to other available Class A poisons. The data obtained from this cross sensitivity testing are given in Table 9. Phosphine at a concentration of 6.1 mg/m^3 (4.3 ppm) gives a positive response, this being an orange ring on a yellow background.

This method appears to be a promising approach for the field detection of mustard gas at hazardous waste sites. However, further laboratory effort should be conducted to establish the parameters of this technique with regard to mustard gas.

TABLE 9. Mustard Gas Detector Tube Interference Data

Gas	Test Gas Concentration mg/m^3	Interference Response
Arsine	152.2(47.7ppm)	No
Cyanogen	106.4(50.0ppm)	No
Germane	187.8(60.0ppm)	No
Hydrogen cyanide	55.2(50.0ppm)	No
Nitric oxide	56.4(46.0ppm)	No
Nitrogen dioxide	82.8(45.0ppm)	No
Phosgene	190.3(47.0ppm)	No
Phosphine	64.5(45.4ppm)	Yes
	6.1(4.3ppm)	Yes
	0.43(0.3ppm)	No

Hydrogen Cyanide

The method which theoretically appears to be the most promising technique for the rapid field screening of hydrogen cyanide, as a result of Phase 1 of this study, was the Draeger hydrogen cyanide detector tube CH25701. Information supplied by the manufacturer states that the tube has a detection range of 2.26 to 33.90 mg/m^3 using a 500ml sample (5 pump strokes). This tube also has a precleanse layer which is supposed to retain potentially interfering acidic or basic gases. The relative standard deviation of the tube was reported to be 10 to 15 percent.

Laboratory testing of this tube was conducted at hydrogen cyanide concentrations of 5.5, 10.5, and 20.4 mg/m^3 using 500ml samples and each concentration was tested in triplicate. The threshold limit value for hydrogen cyanide is 11.0 mg/m^3 for an eight hour exposure. The data obtained from these three concentrations are given in Table 10 and shown graphically in Figure 4. As can be seen from the statistical values in Table 10 the reproducibility of the data gave coefficients of variance between 0 and 16 percent. The average percent difference calculated between the experimental data and preprinted tube scale curves was 9. This curve and the calculated percent difference indicates that this method is capable of detecting semi-quantitatively at concentrations in the range of 5 to 20 mg/m^3.

The literature supplied by Draeger also stated that the tube is capable of detecting 5.5 to 82.8 mg/m^3 of the gas with sample volumes of 200ml (2 pump strokes). To evaluate this concentration range using the reduced sample volume Atlantic Research Corporation tested four different concentrations. Hydrogen cyanide was sampled in triplicate at concentrations of 10.5, 30.9, 45.3 and 55.2 mg/m^3. The results of this testing are given in Table 11 and illustrated graphically in Figure 5. The reproducibility of tests conducted using a 2 pump stroke sample volume were comparable to those using a 5 pump stroke sample. The accuracy of this detection technique, calculated by the average percent difference for the experimental curve and the extrapolated preprinted scale curve was 42. The data obtained from these tests indicates that this tube, using only two pump strokes, is capable of distinguishing increasing hydrogen cyanide concentrations in the range of 10 to 55.2 mg/m^3. However, it would appear that the tube scale needs to be modified to permit more accurate semi-quantitative analysis.

Atlantic Research Corporation tested this detector tube for cross sensitivity to the other available Class A poisons. The data obtained from these tests are given in Table 12. Three additional Class A poisons are detected by this method, they are arsine, cyanogen and phosphine. The detection of this tube is based on the reaction of hydrocyanic acid with mercuric chloride, the acid liberated (HCl) then reacts with the methyl red indicating layer. Although this tube employs a precleanse layer to remove acidic or basic interfering gases, the capabilities of this layer seem to be limited to low concentrations of acidic or basic gases based on the interference studies. In addition it appears that any gas capable of forming HCl from its reaction with mercuric chloride will produce a positive interference. Further laboratory evaluation is necessary to determine the extent of interferences for this technique.

TABLE 10. HYDROGEN CYANIDE DETECTION TUBE (1 ppm = 1.104 mg/m^3)

	TEST 1		TEST 2		TEST 3	
Experimental Parameters						
Actual test conc. (ppm)	5.0 (5.5 mg/m^3)		9.5 (10.5 mg/m^3)		18.5 (20.4 mg/m^3)	
Number of pump strokes	5		5		5	
Sample volume (ml)	500		500		500	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3	
	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
TEST DATA	6.0 (6.6 mg/m^3)	16	9.9 (10.9 mg/m^3)	23	20.0 (22.1 mg/m^3)	37
	8.0 (8.8 mg/m^3)	18	9.9 (10.9 mg/m^3)	23	16.0 (17.7 mg/m^3)	31
	8.0 (8.8 mg/m^3)	18	9.9 (10.9 mg/m^3)	23	19.0 (21.0 mg/m^3)	36
STATISTICAL						
MEAN	$\bar{X}$ = 7.3 (8.0 mg/m^3)		$\bar{X}$ = 9.9 (10.9 mg/m^3)		$\bar{X}$ = 18.3 (20.2 mg/m^3)	
STANDARD DEVIATION	S_d = 1.15		S_d = 0.0		S_d = 2.08	
COEFFICIENT OF VARIANCE	C_v = 0.16		C_v = 0.0		C_v = 0.11	

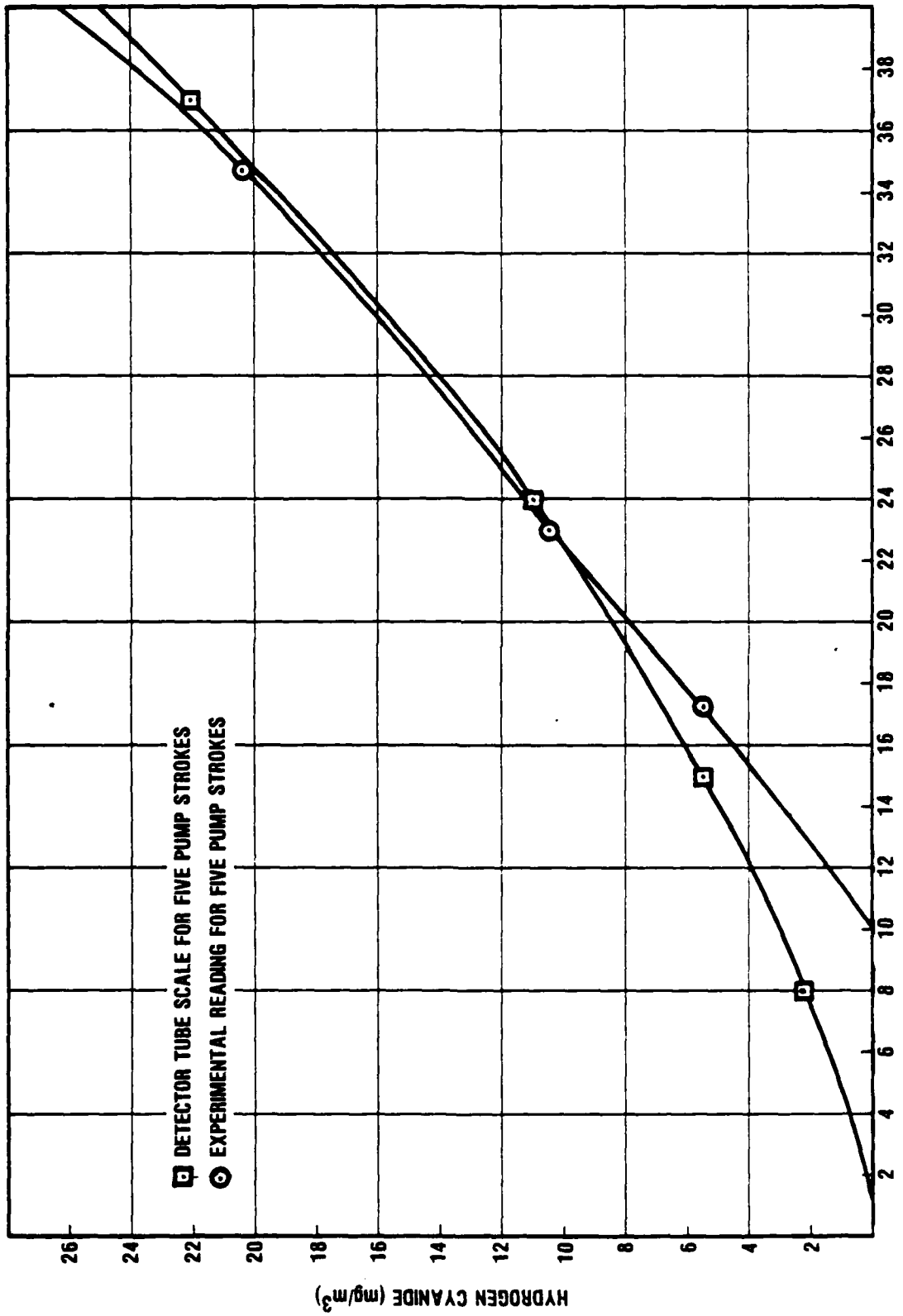

Figure 4. Stain Length Versus Hydrogen Cyanide Concentration (with 5 pump strokes).

TABLE 11. HYDROGEN CYANIDE DETECTION TUBE (ppm = 1.104 mg/m^3)

	TEST 1		TEST 2		TEST 3		TEST 4	
Experimental parameters								
Actual test conc. (ppm)	9.5 (10.5 mg/m^3)		28.0 (30.9 mg/m^3)		41.0 (45.3 mg/m^3)		50.0 (55.2 mg/m^3)	
Number of pump strokes	2		2		2		2	
Sample volume (ml)	200		200		200		200	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3		RESULTS TEST 4	
	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
TEST DATA	10.0 (11.0 mg/m^3)	13	20.0 (22.1 mg/m^3)	18	25.0 (27.6 mg/m^3)	24	37.5 (41.4 mg/m^3)	36
	7.50 (8.28 mg/m^3)	11	20.0 (22.1 mg/m^3)	18	30.0 (33.1 mg/m^3)	27	50.0 (55.2 mg/m^3)	38
	8.75 (9.66 mg/m^3)	12	20.0 (22.1 mg/m^3)	18	28.5 (31.5 mg/m^3)	26	50.0 (55.2 mg/m^3)	38
STATISTICAL								
MEAN	$\bar{X}$ = 8.75 (9.66 mg/m^3)		$\bar{X}$ = 20.0 (22.1 mg/m^3)		$\bar{X}$ = 27.8 (30.7 mg/m^3)		$\bar{X}$ = 45.8 (50.6 mg/m^3)	
STANDARD DEVIATION	S_d = 1.25		S_d = 0.0		S_d = 2.6		S_d = 7.2	
COEFFICIENT OF VARIANCE	C_v = 0.14		C_v = 0.0		C_v = 0.09		C_v = 0.16	

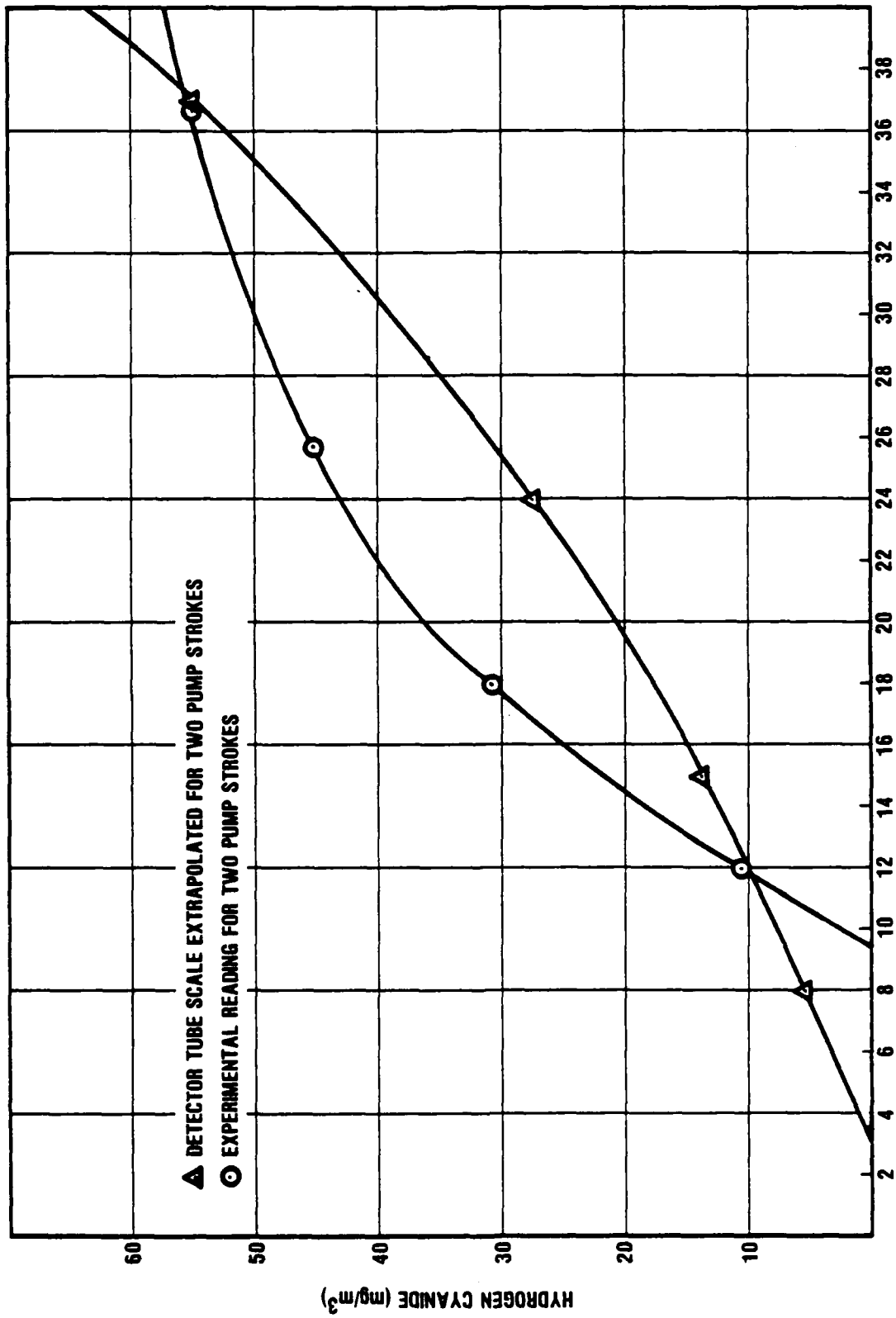

Figure 5. Stain Length Versus Hydrogen Cyanide Concentration (with 2 pump strokes).

TABLE 12. Hydrogen Cyanide Detector Tube Interference Data

Gas	Test Gas Concentration - mg/m^3	Interference Response
Arsine	152.2 (47.7ppm)	Yes
	10 (3.1ppm)	Yes
	0.16 (0.05ppm)	No
Cyanogen	106.4 (50.0ppm)	Yes
	22.0 (10.3ppm)	No
Germane	187.8 (60.0ppm)	No
Nitric Oxide	56.4 (46.0ppm)	No
Nitrogen Dioxide	82.8 (45.0ppm)	No
Phosgene	190.3 (47.0ppm)	No
Phosphine	64.5 (45.4ppm)	Yes
	0.43 (0.3ppm)	No

Dichloro (2-chlorovinyl) arsine (lewisite)

The candidate method which theoretically appears to be the most promising for the field detection of lewisite is the Michler's thioketone reagent system. This method is used by the United States Army in the M-256 War Gas Detection Kit for the detection of lewisite. However, it is not commercially available. Atlantic Research Corporation contacted Draegerwerk (Germany) and found that they produce a tube capable of detecting arsine, phosphine, lewisite, methyldichloroarsine and ethyldichloroarsine. This tube (lewisite and arsine tube CH26303) although presently not commercially available could be obtained by special ordering arrangements with Draegerwerk (Germany). Atlantic Research Corporation arranged to receive several boxes of these tubes for evaluation purposes in our laboratory.

The information supplied by Draeger, along with samples of their lewisite/arsine detector tubes, stated that arsine and phosphine are detected with a sensitivity of approximately 0.3 mg/m^3 using an 800ml sample. Lewisite, methyldichloroarsine and ethyldichloroarsine are detected with a sensitivity of approximately 3 mg/m^3 also using an 800ml sample. Due to the unavailability of lewisite, ethyldichloroarsine and methyldichloroarsine standard gas mixtures Atlantic Research Corporation was not able to verify these detection limits within the time constraints of this program. However, detection limits testing for arsine and phosphine were conducted. Arsine was detected at a level of 10 mg/m^3 but not at 0.16 mg/m^3, which is its TLV, using an 800ml sample (8 pump strokes) while phosphine was detected at a level of 6.1 mg/m^3 but not at 0.61 mg/m^3, which is its TLV, using an eight pump stroke sample.

The Draeger lewisite and arsine detector was also tested for any cross sensitivity to the other available Class A poisons. The results obtained from this cross sensitivity testing are given in Table 13. No other Class A poison tested interfered with this tube.

This technique appears to be the most promising method, because of its availability, for the field detection of lewisite, ethyldichloroarsine and methyldichloroarsine. It may also be used for the detection of arsine and phosphine at low concentrations of these gases. However, this technique does not offer the sensitivity of those tubes manufactured for the specific detection of these two gases and will not detect them at their TLV concentrations.

TABLE 13. Lewisite and Arsine Gas Detector Tube Interference Data

Gas	Concentration mg/m^3	Interference w/t Tube
Cyanogen	106.4(50.0ppm)	No
Germane	187.8(60.0ppm)	No
Hydrogen cyanide	55.2(50.0ppm)	No
Nitric oxide	56.4(46.0ppm)	No
Nitrogen dioxide	82.8(45.0ppm)	No
Phosgene	190.3(47.0ppm)	No
Phosphine	64.5(45.4ppm)	No

Nitric Oxide

The method which appears to be the most advantageous for the rapid field screening of nitric oxide, as a result of Phase 1 of this study is the Draeger nitrous fumes detector tube CH29401. This tube will detect both nitric oxide and nitrogen dioxide. Since the latter gas is also a Class A poison both gases can be screened simultaneously. To determine the specific presence of nitric oxide the operator, upon confirmation of the presence of nitric oxide and/or nitrogen dioxide, would use the Draeger nitrogen dioxide detector tube. Thus, the nitric oxide concentration may be determined by the difference in the reading of the two types of tubes. Manufacturer's literature supplied along with the nitrous fumes detector tube state that the range of measurement of this tube is from 0.5 to 10 ppm ($NO + NO_2$) using a 500 ml sample (5 pump strokes). Listed interferences for this tube are ozone and chlorine but these gases react with reduced sensitivity.

Laboratory testing of this tube was conducted at nitric oxide concentrations of 1.67 mg/m^3, 4.90 mg/m^3, and 6.75 mg/m^3 using 5 pump strokes, and 20 mg/m^3, 33 mg/m^3, add 56 mg/m^3 using one pump stroke. Each of these concentrations was sampled in triplicate. The threshold limit value of nitric oxide exposure for an eight hour period is 31.25 mg/m^3. The results of those concentrations using a 5 pump stroke sample are given in Table 14 and shown graphically in Figure 6 . The reproducibility of this tube using a five pump stroke sample volume was excellent. The average percent difference between the experimental and preprinted tube scale curves was calculated to be 14. Figure 6 indicates that the percent difference decreases as the concentration increases. Even though the percent difference seems high it is possible to conclude from the curves that the nitrous fumes detector tube detects semi-quantitatively.

Draeger did not specify that the nitrous fumes tube detectable range could be expanded by varying the sample volume. However, in order to evaluate the threshold limit value for nitric oxide (31.25 mg/m^3) it was necessary to reduce the recommended sample volume from 500 ml to 100 ml. The results of experimentation using the reduced sample volumes for higher concentrations of nitric oxide are given in Table 15 and shown graphically in Figure 7. This technique, to expand to detectable range, produced very reproducible results with the exception of the 56 mg/m^3 concentration which had a coefficient of variance of 0.113. The average percent difference between the extrapolated and experimental curve was calculated to be 20. After examining the curves in Figure 7 it appears that this method of expanding the tube scale is not accurate for the measurement of nitric oxide in the concentration range of 20 to 56 mg/m^3.

In summary, examination of the experimental data indicates that when using a 500 ml sample containing low concentrations of nitric oxide the technique will detect the gas semi-quantitatively. However, when using a smaller (100 ml) sample the tube scale does not appear accurate for measuring in the concentration range of 20 to 56 mg/m^3. The tube, however, will indicate increasing concentrations of nitric oxide.

TABLE 14. NITROUS FUMES DETECTION TUBE (1 ppm = 1.227 mg/m^3)

	TEST 1		TEST 2		TEST 3	
Experimental Parameters						
Actual test conc. (ppm)	1.36 (1.67 mg/m^3)		3.99 (4.90 mg/m^3)		5.50 (6.75 mg/m^3)	
Number of pump strokes	5		5		5	
Sample volume (ml)	500		500		500	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3	
TEST DATA	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
	1.90 (2.3 mg/m^3)	16.0	4.30 (5.28 mg/m^3)	31	6.0 (7.4 mg/m^3)	37
	1.95 (2.39 mg/m^3)	17.5	4.30 (5.28 mg/m^3)	31	6.0 (7.4 mg/m^3)	37
	1.95 (2.39 mg/m^3)	17.5	4.30 (5.28 mg/m^3)	31	6.0 (7.4 mg/m^3)	37
STATISTICAL						
MEAN	$\bar{X}$ =1.93(2.37 mg/m^3)		$\bar{X}$ = 4.30 (5.28 mg/m^3)		$\bar{X}$ = 6.0 (7.4 mg/m^3)	
STANDARD DEVIATION	S_d = 0.029		S_d = 0.0		S_d = 0.0	
COEFFICIENT OF VARIANCE	C_v = 0.015		C_v = 0.0		C_v = 0.0	

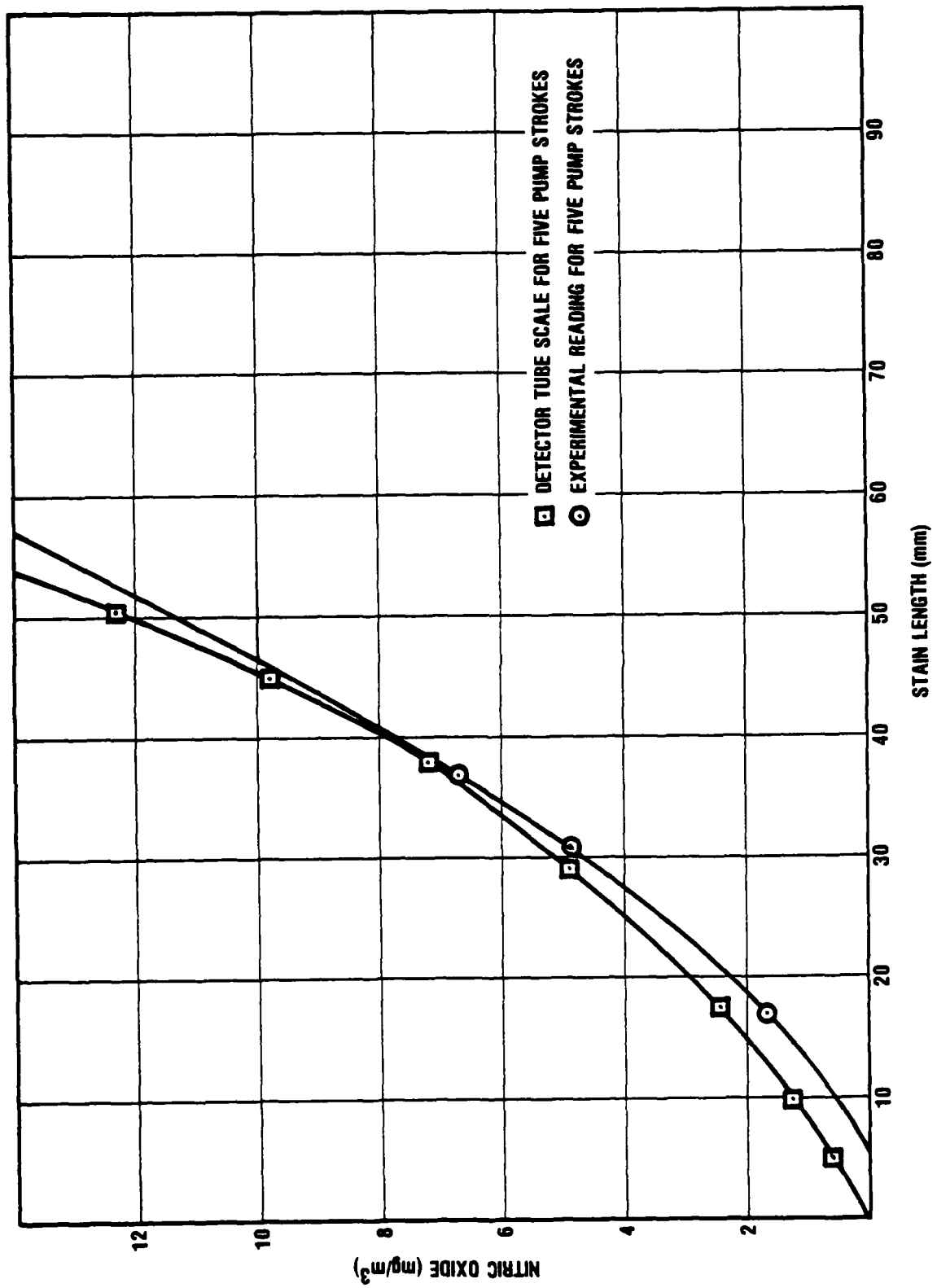

Figure 6. Stain Length Versus Nitric Oxide Concentration (with 5 pump strokes).

TABLE 15. NITROUS FUMES DETECTION TUBE (1 ppm = 1.227 mg/m^3)

	TEST 1		TEST 2		TEST 3	
Experimental Parameters						
Actual test conc. (ppm)	16 (20 mg/m^3)		27 (33 mg/m^3)		46 (56 mg/m^3)	
Number of pump strokes	1		1		1	
Sample volume (ml)	100		100		100	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3	
TEST DATA	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
	11 (13 mg/m^3)	18	15 (18 mg/m^3)	25	40 (49 mg/m^3)	48
	11 (13 mg/m^3)	18	15 (18 mg/m^3)	25	35 (43 mg/m^3)	42
	11 (13 mg/m^3)	18	15 (18 mg/m^3)	25	32 (39 mg/m^3)	40
STATISTICAL						
MEAN	$\bar{X}$ = 11 (13 mg/m^3)		$\bar{X}$ = 15 (18 mg/m^3)		$\bar{X}$ = 35.7 (44 mg/m^3)	
STANDARD DEVIATION	S_d = 0.0		S_d = 0.0		S_d = 4.04	
COEFFICIENT OF VARIANCE	C_v = 0.0		C_v = 0.0		C_v = 0.11	

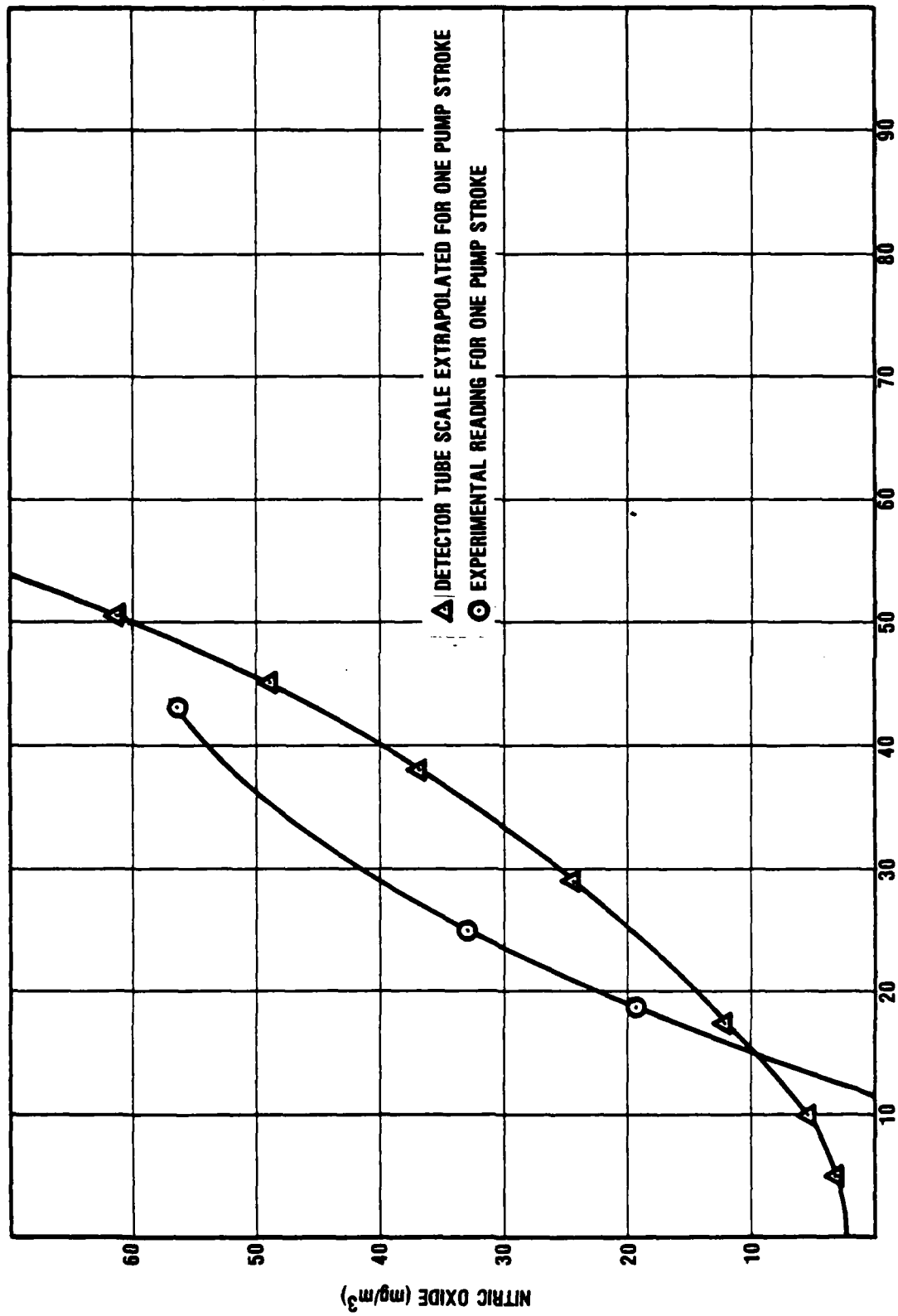

Figure 7. Stain Length Versus Nitric Oxide Concentration (with 1 pump stroke).

Atlantic Research tested this tube for any cross sensitivities with the other available Class A poisons. The results of this cross sensitivity testing are given in Table 16. The only other Class A poison detected by this method is nitrogen dioxide, at its TLV of 9.0 mg/m^3 (4.89 ppm), which the tube is designed to detect.

The data obtained from laboratory evaluation of this method indicates that this tube is capable of detecting nitric oxide at its threshold limit value. The tube appears to be a promising method for the field screening of nitric oxide, although at higher concentrations of the gas semi-quantitative readings are not reliable.

TABLE 16. Nitrous Fumes Detector Tube Interference Data

Gas	Test Gas Concentration	Interference Response
Arsine	152.2 (47.7 ppm)	No
Cyanogen	106.4 (50.0 ppm)	No
Germane	187.8 (60.0 ppm)	No
Hydrogen Cyanide	55.2 (50.0 ppm)	No
Nitrogen dioxide	82.8 (45.0 ppm)	Yes
	18.4 (10.0 ppm)	Yes
	9.0 (4.89 ppm)	Yes
Phosgene	190.3 (47.0 ppm)	No
Phosphine	64.5 (45.4 ppm)	No

Nitrogen dioxide

The technique which appears to be best suited for the field detection of nitrogen dioxide, based on Phase I of this study, is the Draeger nitrogen dioxide detector tube CH30001. Literature supplied by Draeger describes that this tube has a range of detection of 0.5 to 10 ppm with a 500ml sample volume and from 5 to 25 ppm with a 200ml sample volume. Ozone and chlorine are listed as interferences for this tube but react with a reduced response.

Laboratory evaluation of the limits of detection for this method was conducted at concentrations of 1.77 mg/m^3, 7.30 mg/m^3 and 14.8 mg/m^3 for 500ml samples and 9.0 mg/m^3, 18.4 mg/m^3 and 46.0 mg/m^3 for samples containing 200ml volumes. Each of these concentrations was examined in triplicate. The threshold limit value for an eight hour exposure to nitrogen dioxide is 9.0 mg/m^3. The results of testing those concentrations, using a 500ml sample, are given in Table 17 and illustrated graphically in Figure 8. Examination of this data indicates that the Draeger nitrogen dioxide detector tube can be used for the semi-quantitative determination of this gas at low concentrations (1.8 mg/m^3 to 15 mg/m^3) using a five pump stroke sample. The data, as obtained from the triplicate sampling, indicates that at these concentrations and sample volumes the results are very reproducible. In addition, the average percent differences between the curve generated from experimental data and the curve obtained by plotting hypothetical stain lengths from the preprinted scale values is 0.54. On the basis of these results, it appears that the nitrogen dioxide detector tube is extremely accurate using a 5 pump stroke sample volume.

Results for those concentrations using a two pump stroke sample volume are given in Table 18 and shown graphically in Figure 9. These results indicate that the data obtained are very reproducible for concentrations under 20 mg/m^3. At the concentration of 46 mg/m^3 one sample deviated from the other two taken by 3mm in stain length. This deviation could have been the result of operator error in taking the sample, mismeasurement of the stain length or a function of the detector tube. Further testing needs to be conducted at this higher gas concentraion before a definite account can be given for the reproducibility of this tube at concentrations in excess of 20 mg/m^3. This data also agrees with the preprinted concentration scale on the Draeger tube for concentrations below 20 mg/m^3. However, when concentrations of nitrogen dioxide are in excess of 20 mg/m^3 it appears that comparing stain lengths to concentration marks on the tube is unreliable. Further laboratory effort needs to be conducted between 20 mg/m^3 and 50 mg/m^3 concentrations to determine the actual performance capabilities of this tube at these concentrations using 200ml sample volumes.

Atlantic Research Corporation investigated the possibility of cross interferences by other Class A poisons with this tube. This interference data was conducted using 500ml sample volumes of the potential interfering gases. The results of this testing are given in Table 19. No other Class A poison interfered with this technique.

TABLE 17. NITROGEN DIOXIDE DETECTION TUBE (1 ppm = 1.84 mg/m^3)

	TEST 1		TEST 2		TEST 3	
Experimental Parameters						
Actual test conc. (ppm)	0.96 (1.77 mg/m^3)		3.97 (7.30 mg/m^3)		8.05 (14.8 mg/m^3)	
Number of pump strokes	5		5		5	
Sample volume (ml)	500		500		500	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3	
TEST DATA	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
	0.96 (1.77 mg/m^3)	11	4.0 (7.4 mg/m^3)	30	8.00 (14.7 mg/m^3)	44
	0.96 (1.77 mg/m^3)	11	4.0 (7.4 mg/m^3)	30	7.95 (14.6 mg/m^3)	43
	0.96 (1.77 mg/m^3)	11	4.0 (7.4 mg/m^3)	30	8.00 (14.7 mg/m^3)	44
STATISTICAL						
MEAN	$\bar{X}$ =0.96(1.77 mg/m^3)		$\bar{X}$ = 4.0 (7.4 mg/m^3)		$\bar{X}$ = 7.98(14.7 mg/m^3)	
STANDARD DEVIATION	S_d = 0.0		S_d = 0.077		S_d = 0.03	
COEFFICIENT OF VARIANCE	C_v = 0.0		C_v = 0.0		C_v = 0.004	

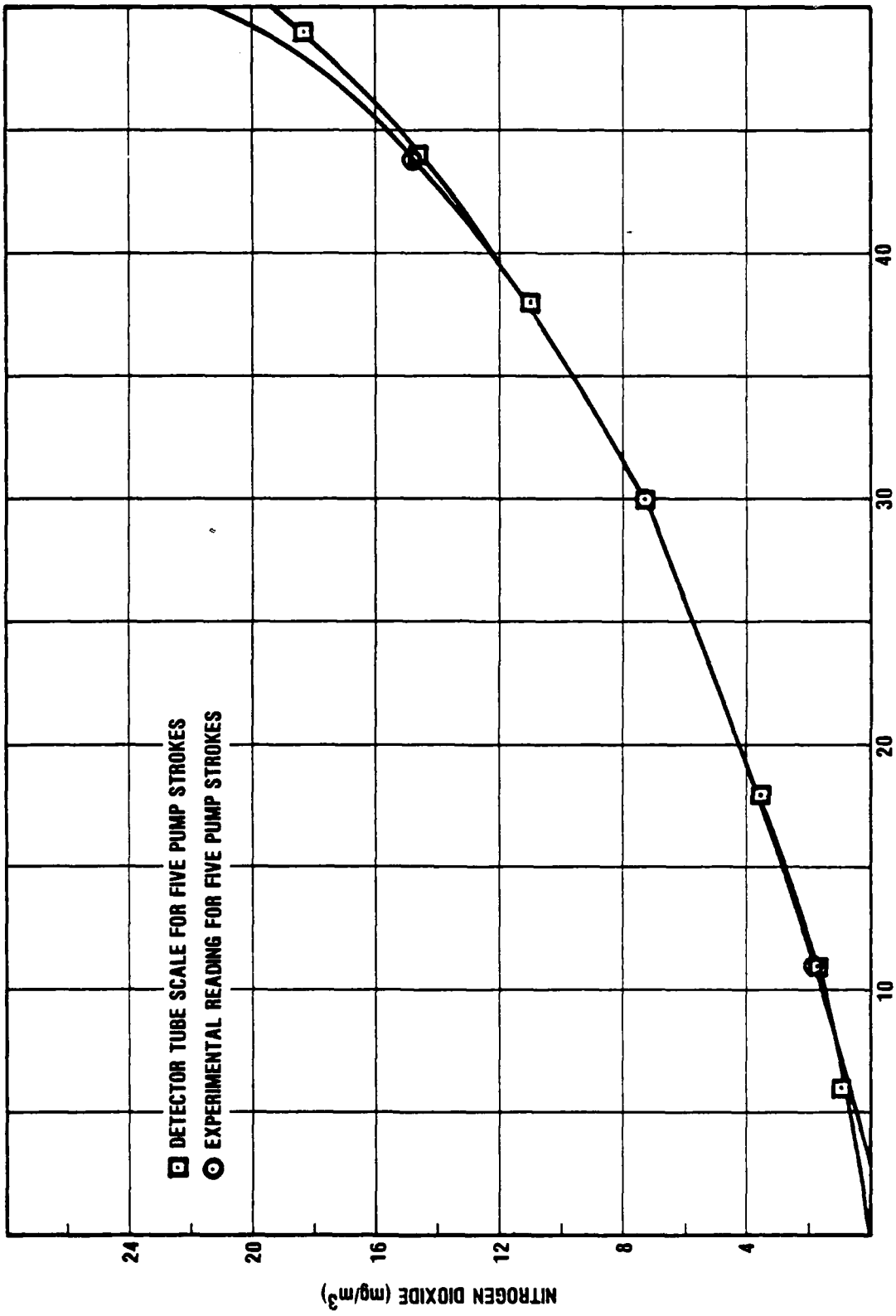

Figure 8. Stain Length Versus Nitrogen Dioxide Concentration (with 5 pump strokes).

TABLE 18. NITROGEN DIOXIDE DETECTION TUBE (1 ppm = 1.84 mg/m^3)

	TEST 1		TEST 2		TEST 3	
Experimental Parameters						
Actual test conc. (ppm)	4.9 (9.0 mg/m^3)		10 (18.4 mg/m^3)		25 (46.0 mg/m^3)	
Number of pump strokes	2		2		2	
Sample volume (ml)	200		200		200	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3	
TEST DATA	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
	5.0 (9.0 mg/m^3)	16	11.0 (20.2 mg/m^3)	27	15.0 (27.6 mg/m^3)	34
	5.0 (9.0 mg/m^3)	16	11.0 (20.2 mg/m^3)	28	20.0 (36.8 mg/m^3)	37
	5.0 (9.0 mg/m^3)	16	11.0 (20.2 mg/m^3)	27	20.0 (36.8 mg/m^3)	37
STATISTICAL						
MEAN	$\bar{X}$ = 5.0(9.0 mg/m^3)		$\bar{X}$ = 11.0 (20.2 mg/m^3)		$\bar{X}$ = 18.3(33.7 mg/m^3)	
STANDARD DEVIATION	S_d = 0.0		S_d = 0.0		S_d = 2.9	
COEFFICIENT OF VARIANCE	C_v = 0.0		C_v = 0.0		C_v = 0.16	

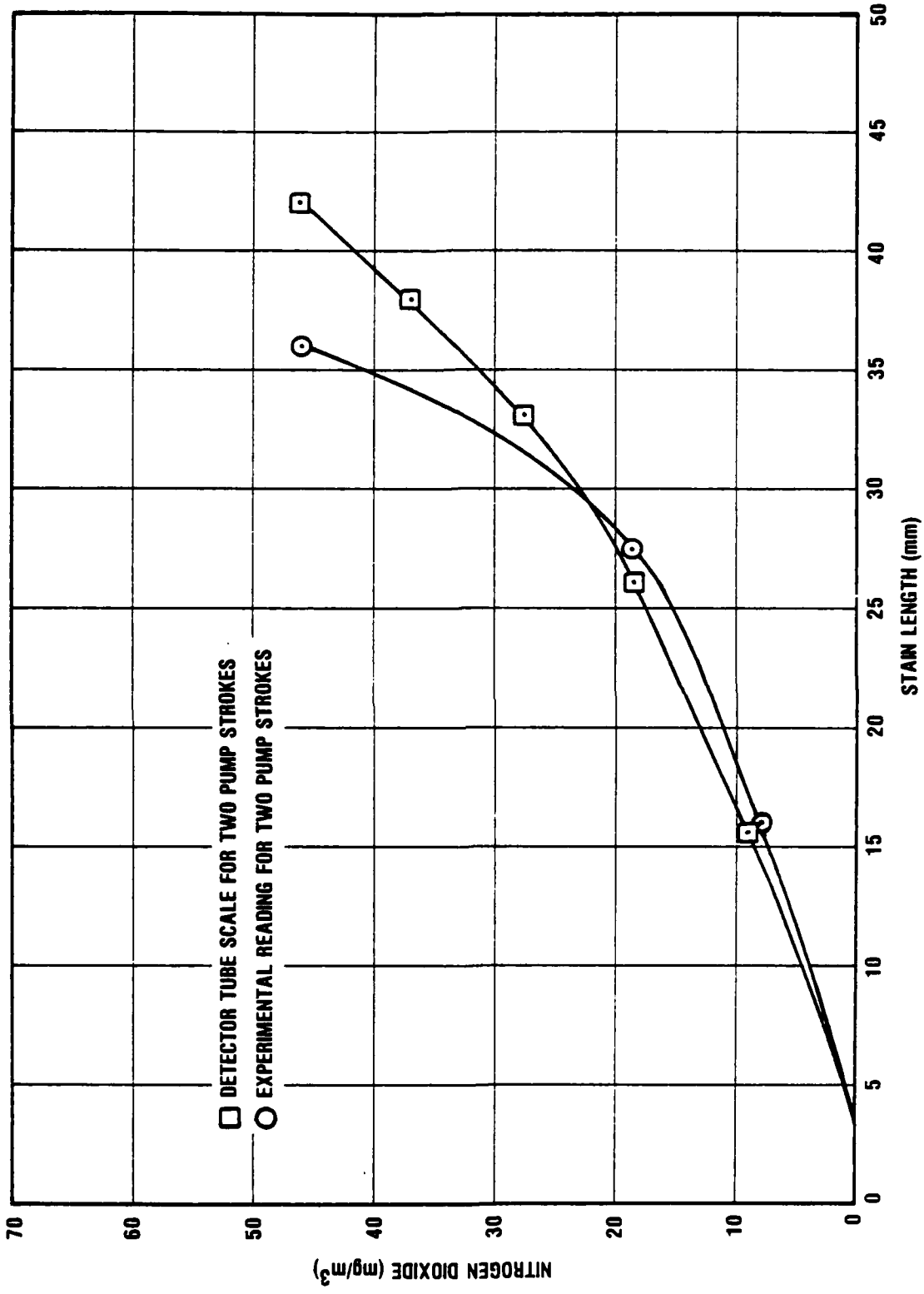

Figure 9. Stain Length Versus Nitrogen Dioxide Concentration (with 2 pump strokes).

TABLE 19. Nitrogen Dioxide Detection Tube Interference Data

Gas	Test Gas Concentration - mg/m^3	Interference Response
Arsine	152.2(47.7ppm)	No
Cyanogen	106.4(50.0ppm)	No
Germane	187.8(60.0ppm)	No
Hydrogen cyanide	55.2(50.0ppm)	No
Nitric oxide	56.4(46.0ppm)	No
Phosgene	190.3(47.0ppm)	No
Phosphine	64.5(45.4ppm)	No

The Draeger nitrogen dioxide detector tube CH30001 appears to be a promising method for the field detection of this gas. This tube is able to accurately detect 9 mg/m^3, the threshold limit value, of this gas using either a 500 or 200ml sample volume. However, further laboratory research needs to be conducted to determine if this technique can be used for semi-quantitative determination at concentrations above 20 mg/m^3.

Phosgene

The method which appears to be the most promising technique for the rapid field detection of phosgene is the Draeger phosgene detector tube CH19401. Information supplied by Draeger indicates that this tube has a measurable range of 0.12 to 4.96 mg/m^3 using sample volumes of 100 to 2,600ml (1 to 26 pump strokes) with a reported relative standard deviation of 15 to 20 percent. Interferences for this detection method are carbonyl bromide and acetyl chloride. This tube contains a color-comparison layer, and an indicating layer. When testing for phosgene the test is completed when the color of the indicating layer matches that of the color comparison layer or 26 pump strokes are taken and no color change is noted in the indicating layer. To determine the concentration of phosgene the number of pump strokes necessary to reach identical coloration of the indicating and comparison layers is compared to a supplied preprinted table.

Phosgene was sampled at concentrations of 0.4 mg/m^3, 0.73 mg/m^3, 2.0 mg/m^3 and 4.05 mg/m^3. The threshold limit value of this gas corresponds to the 0.4 mg/m^3 concentration. The data obtained from this testing are given in Table 20 and shown graphically in Figure 10. It must be noted that it is difficult to determine when the end point has been reached. The color change indicating the presence of phosgene, however, is easy to observe. This laboratory continued to draw pump strokes through the detector tube until no further color intensity change was noted. At this point the final pump stroke was subtracted from the total number of pump strokes taken. This approach allowed a degree of certainly that the actual end point had been reached. The reproducibility of this technique, as can be determined from the standard deviation and coefficient of variance in Table 20, is extremely good. The average percent difference of the experimental and tube scale curves was calculated to be 4.

Cross sensitivies of other Class A poisons with this detector tube were investigated. The results of the cross-sensitivity testing during the evaluation of the Draeger phosgene detector tube are given in Table 21. The only Class A poison which cross reacted with this tube was nitrogen dioxide at a concentration of 82.8 mg/m^3 in a sample volume of 1400ml. The color change which occurred at this concentration was not the same reaction as would be obtained if phosgene was present. The indicating layer turned from a pale yellow to a very bright yellow, while phosgene produces a color change from pale yellow to a light green. This different coloration of the indicating layer may produce a negative interference. The evaluation data obtained with this technique indicates that this method is a rapid, sensitive, and relatively accurate means of screening for phosgene at concentration equal or above the TLV of this gas.

TABLE 20. PHOSGENE DETECTION TUBE (1 ppm = 4.05 mg/m^3)

	TEST 1		TEST 2		TEST 3		TEST 4	
Experimental parameters								
Actual test conc. (ppm)	0.1 (0.4 mg/m^3)		0.18 (0.73 mg/m^3)		0.5 (2.0 mg/m^3)		1.0 (4.05 mg/m^3)	
Number of pump strokes	16		8		3		2	
Sample volume (ml)	1600		800		300		200	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3		RESULTS TEST 4	
	TUBE SCALE (ppm)	NUMBER OF PUMP STROKES	TUBE SCALE (ppm)	NUMBER OF PUMP STROKES	TUBE SCALE (ppm)	NUMBER OF PUMP STROKES	TUBE SCALE (ppm)	NUMBER OF PUMP STROKES
TEST DATA	0.085 (0.344 mg/m^3)	16	0.18 (0.73 mg/m^3)	8	0.5 (2.0 mg/m^3)	3	0.75 (3.03 mg/m^3)	2
	0.085 (0.344 mg/m^3)	16	0.18 (0.73 mg/m^3)	8	0.5 (2.0 mg/m^3)	3	0.75 (3.03 mg/m^3)	2
	0.085 (0.344 mg/m^3)	16	0.18 (0.73 mg/m^3)	8	0.5 (2.0 mg/m^3)	3	0.75 (3.03 mg/m^3)	2
STATISTICAL								
MEAN	$\bar{X}$ = 0.085 (0.344 mg/m^3)		$\bar{X}$ = 0.18 (0.73 mg/m^3)		$\bar{X}$ = 0.5 (2.0 mg/m^3)		$\bar{X}$ = 0.75 (3.03 mg/m^3)	
STANDARD DEVIATION	S_d = 0.0		S_d = 0.0		S_d = 0.0		S_d = 0.0	
COEFFICIENT OF VARIANCE	C_v = 0.0		C_v = 0.0		C_v = 0.0		C_v = 0.0	

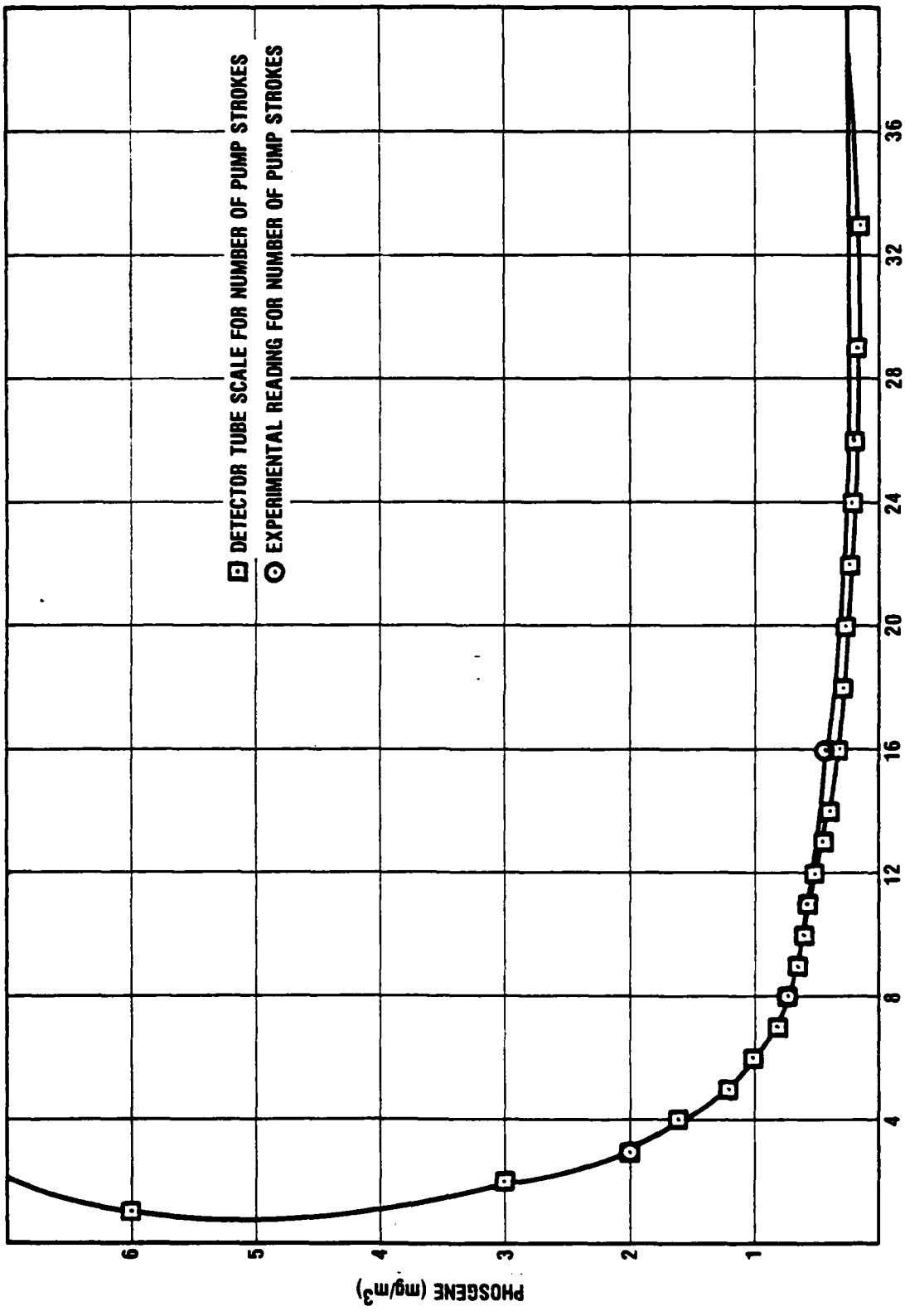

Figure 10. Pump Strokes Versus Phosgene Concentration.

TABLE 21. Phosgene Detector Tube Interference Data

Gas	Concentration	Interference with Tube
Arsine	152.2(47.7ppm)	No
Cyanogen	106.4(50.0ppm)	No
Germane	187.8(60.0ppm)	No
Hydrogen cyanide	55.2(50.0ppm)	No
Nitric oxide	56.4(46.0ppm)	No
Nitrogen dioxide	82.8(45.0ppm)	Yes *
	18.4(10.0ppm)	No
Phosphine	64.5(45.4ppm)	No

* With 14 pump strokes the indicating layer turned a bright yellow. This is not the same colorimetric reaction as would be obtained using phosgene. However, it may interefere with results obtained during phosgene testing. The different coloration of the indicating layer may produce a negative interference.

Phosphine

The method determined in Phase I of this study, which appears to be the most advantageous for the rapid field screening of phosphine is the Draeger phosphine detector tube CH31101. Draeger's literature concerning this tube states that it has a measurable range of 0.14 to 5.68 mg/m^3 using a 10 pump stroke sample volume with a relative standard deviation of 15 to 20 percent. Listed interferences for this technique are arsine and antimony hydride.

Evaluation of this detector tube was conducted at concentrations of 0.43 mg/m^3, 0.61 mg/m^3, 3.1 mg/m^3 and 6.0 mg/m^3 using a sample volume of 1,000ml (10 pump strokes) and 6.1 mg/m^3, 28.2 mg/m^3 and 53.0 mg/m^3 using a one pump stroke sample. The results for those concentrations tested using the 1,000ml sample volume are given in Table 22 and shown graphically in Figure 11. This method appears to be very reproducible, as can be seen from the standard deviation and coefficient of variance values in Table 22. An average percent difference of 7 was calculated from the curves obtained from the experimental data and preprinted tube scale. The data obtained from this experimentation indicates that this technique can detect phosphine at its TLV concentration of 0.43 mg/m^3. In addition, this tube appears to be capable of detecting semi-quantitatively lower concentrations of the gas. However, accuracy tends to decrease as concentrations increase.

Data obtained using higher concentration of phosphine and a sample volume of 100ml are given in Table 23 and shown graphically in Figure 12. This data as can be determined from the standard deviation and coefficient of variance in Table 23, also was very reproducible. An average percent of difference of 20 was obtained between the experimental and calculated curves. These results also indicate that higher concentrations of phosphine can be detected but concentrations not accurately measured using reduced sample volumes. Accuracy decreases, therefore, when comparing an extrapolated (for sample volume) measurement of the preprinted concentration stain lengths to those of increased phosphine concentrations.

The capabilities of this detector tube for detecting other available Class A poisons was examined. The results of this cross sensitivity experimentation are given in Table 24. This data indicates that both arsine and phosphine can be detected using either the Draeger arsine or phosphine detector tube at their TLV concentrations. Arsine detected at 0.16 mg/m^3 (TLV) gave a reading which corresponded to a phosphine reading of 0.14 mg/m^3 as read from the tube scale.

TABLE 22. PHOSPHINE DETECTION TUBE (1 ppm = 1.42 mg/m^3)

	TEST 1		TEST 2		TEST 3		TEST 4	
Experimental parameters								
Actual test conc. (ppm)	0.30 (0.43 mg/m^3)		0.45 (0.61 mg/m^3)		2.2 (3.1 mg/m^3)		4.2 (6.0 mg/m^3)	
Number of pump strokes	10		10		10		10	
Sample volume (ml)	1000		1000		1000		1000	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3		RESULTS TEST 4	
	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
TEST DATA	0.2 (0.3 mg/m^3)	6	0.5 (0.7 mg/m^3)	9	2.5 (3.6 mg/m^3)	30	4.4 (6.2 mg/m^3)	53
	0.2 (0.3 mg/m^3)	6	0.5 (0.7 mg/m^3)	9	2.5 (3.6 mg/m^3)	30	4.8 (6.8 mg/m^3)	56
	0.3 (0.4 mg/m^3)	7	0.5 (0.7 mg/m^3)	9	2.6 (3.7 mg/m^3)	32	4.3 (6.1 mg/m^3)	52
STATISTICAL								
MEAN	$\bar{X}$ = 0.23(0.33mg/m^3)		$\bar{X}$ = 0.5 (0.7 mg/m^3)		$\bar{X}$ = 2.53 (3.63 mg/m^3)		$\bar{X}$ = 4.5 (6.4 mg/m^3)	
STANDARD DEVIATION	S_d = 0.06		S_d = 0.0		S_d = 0.06		S_d = 0.26	
COEFFICIENT OF VARIANCE	C_v = 0.26		C_v = 0.0		C_v = 0.02		C_v = 0.06	

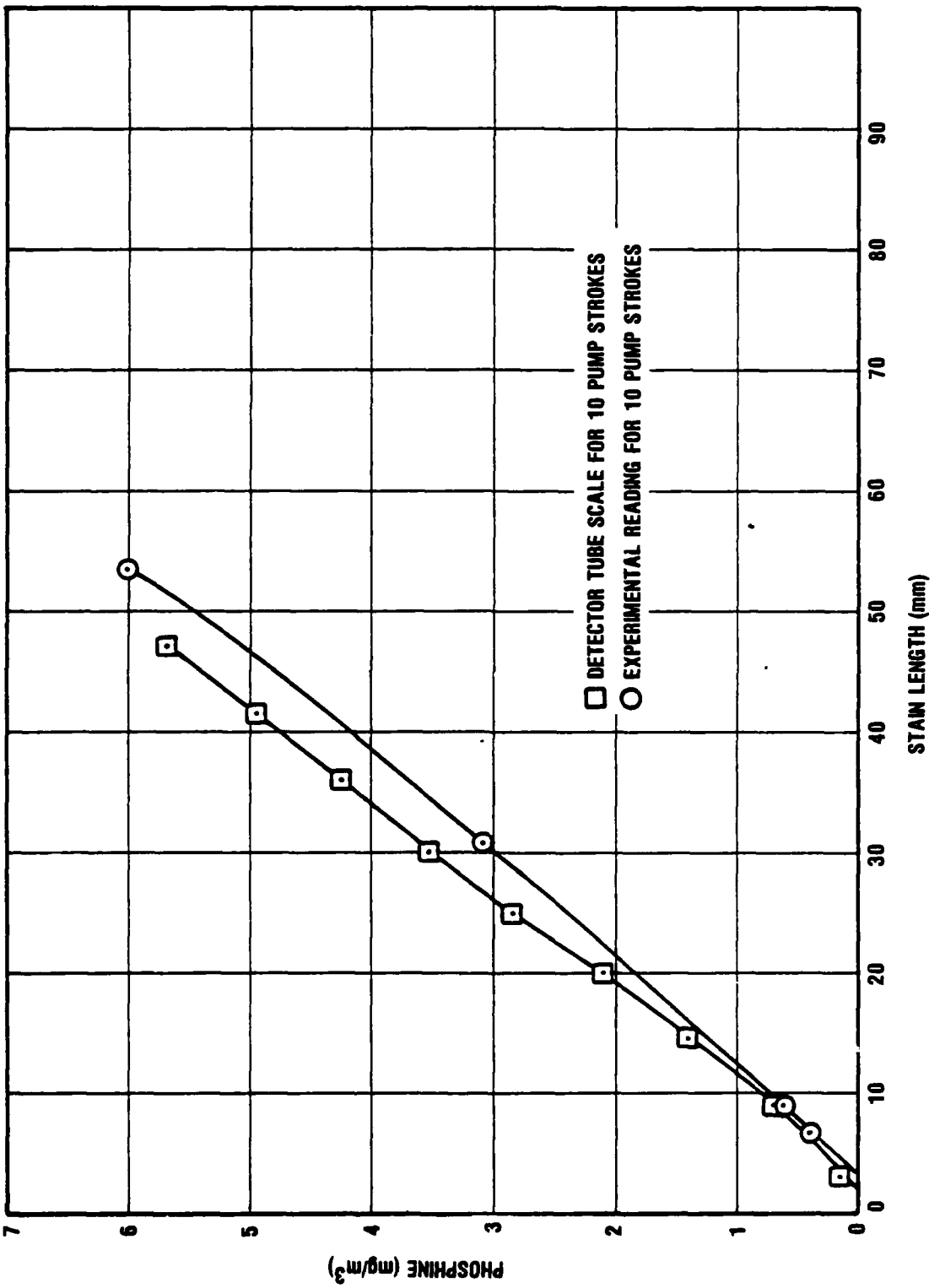

Figure 11. Stain Length Versus Phosphine Concentration (with 10 pump strokes).

TABLE 23. PHOSPHINE DETECTION TUBE (1 ppm ~ 1.42 mg/m^3)

	TEST 1		TEST 2		TEST 3	
Experimental Parameters						
Actual test conc. (ppm)	4.3 (6.1 mg/m^3)		19.9 (28.2 mg/m^3)		37.3 (53.0 mg/m^3)	
Number of pump strokes	1		1		1	
Sample volume (ml)	100		100		100	
	RESULTS TEST 1		RESULTS TEST 2		RESULTS TEST 3	
TEST DATA	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)	TUBE SCALE (ppm)	TUBE STAIN LENGTH (mm)
	5.0 (7.1 mg/m^3)	9	18.0 (25.5 mg/m^3)	24	27 (38.3 mg/m^3)	33
	5.0 (7.1 mg/m^3)	9	16.0 (22.7 mg/m^3)	23	28 (39.8 mg/m^3)	34
	5.0 (7.1 mg/m^3)	9	16.0 (22.7 mg/m^3)	23	29 (41.2 mg/m^3)	35
STATISTICAL						
MEAN	$\bar{X}$ = 5.0(7.1 mg/m^3)		$\bar{X}$ = 16.7 (23.7 mg/m^3)		$\bar{X}$ = 28.0(39.8 mg/m^3)	
STANDARD DEVIATION	S_d = 0.0		S_d = 1.15		S_d = 1.0	
COEFFICIENT OF VARIANCE	C_v = 0.0		C_v = 0.07		C_v = 0.04	

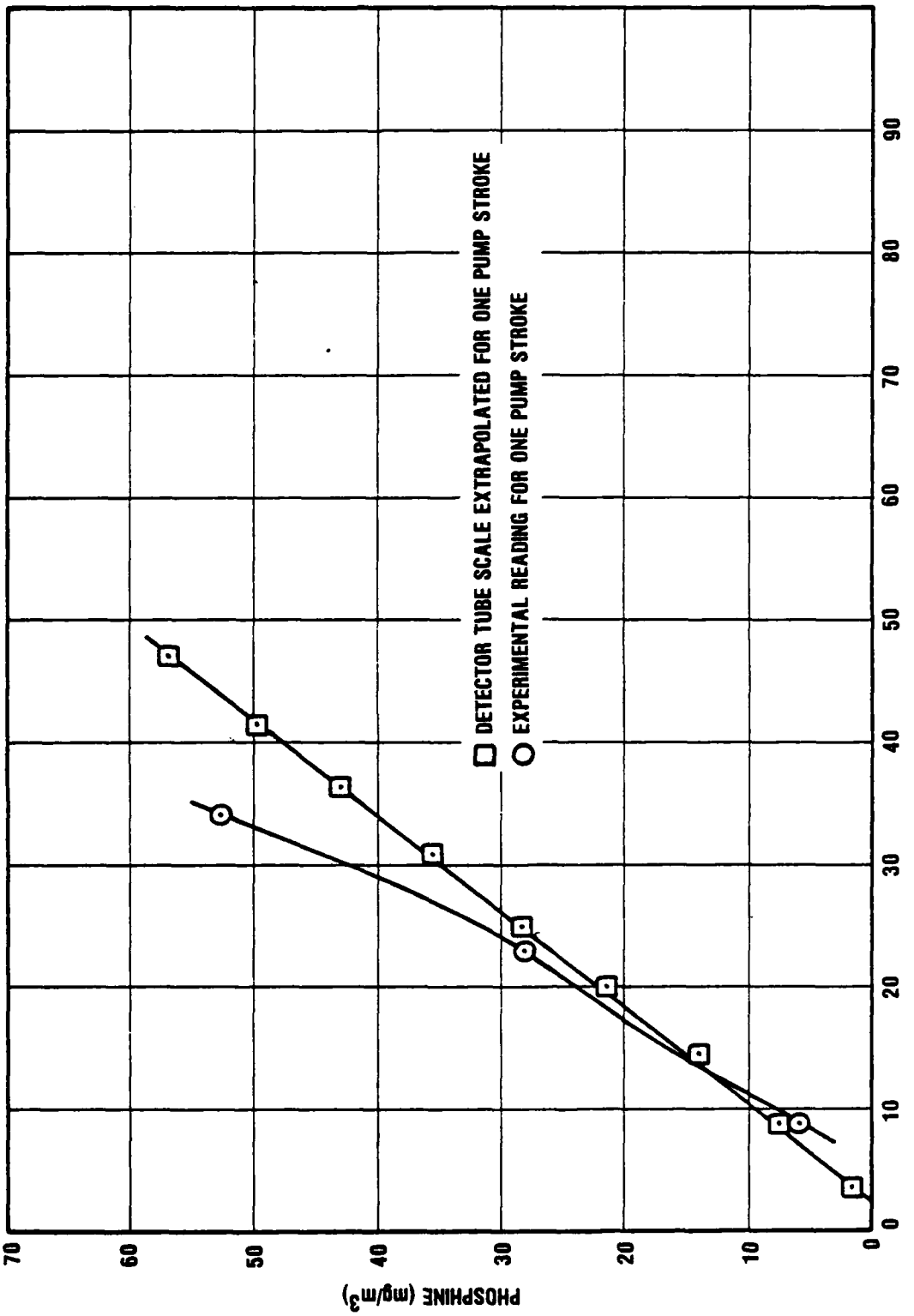

Figure 12. Stain Length Versus Phosphine Concentration (with 1 pump stroke).

TABLE 24. Phosphine Detector Tube Interference Data

Gas	Concentration - mg/m^3	Interference with Tube
Arsine	152.2(47.70ppm)	Yes
	10.0(3.13ppm)	Yes
	0.16(0.05ppm)	Yes
Cyanogen	106.4(50.0ppm)	No
Germane	187.8(60.0ppm)	No
Hydrogen cyanide	55.2(50.0ppm)	No
Nitric oxide	56.4(46.0ppm)	No
Nitrogen dioxide	82.8(45.0ppm)	No
Phosgene	190.3(47.0ppm)	No

END

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